Chemical Composition of Vehicle-Related Volatile Organic Compound Emissions in Central California

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Abstract

Trends in the composition and reactivity of volatile organic compound (VOC) emissions from motor vehicles are described over a 10-year period between 1991 and 2001. Vehicle emissions were measured at the Caldecott tunnel in the San Francisco Bay area in summers 1991, 1994-97, 1999, and 2001. Concurrent liquid gasoline samples were collected from service stations in Berkeley in summers 1995, 1996, 1999, and 2001. Fuel samples were also collected in Sacramento during summer 2001 only. Gasoline headspace vapor composition was calculated using the measured composition of liquid fuel samples and vapor-liquid equilibrium theory. As a result of California's reformulated gasoline (RFG) program, the reactivity of liquid gasoline and headspace vapors were both reduced by ~20%, due mainly to lower aromatic and alkenes in gasoline. The reactivity of tunnel non-methane organic compound (NMOC) emissions decreased by 6% following the introduction of RFG, with reductions in C₉+ aromatics being the most important contributor to this change. Though the reduction in tunnel NMOC reactivity is likely to be helpful, a more important effect through the 1990s has been the significant reduction in the total mass of NMOC emitted by vehicles. After 1996 when Phase 2 RFG requirements first took effect, some refiners began supplying low- or zero-oxygenate gasoline blends in the Bay area. Gasoline samples collected in Sacramento confirm differences in the pattern of oxygenate use between the Bay area and the Central Valley, where Federal RFG program requirements make oxygenate use mandatory. Other related differences include less use of trimethylpentanes in Sacramento vs. Bay area gasoline. In summer 2001, we found only one major gasoline brand using ethanol as an oxygenate; increased reliance on ethanol has occurred since that time due to the phase-out of methyl tert-butyl ether (MTBE) and other ethers in gasoline.

1. Introduction

Volatile organic compounds are important precursors to ozone and secondary particulate matter, which affect both human health and global climate (Seinfeld and Pandis, 1997; IPCC, 2001). The main anthropogenic sources of volatile organic compounds are motor vehicle-related, with significant additional emissions arising from solvent use in paints, consumer products, and industrial processes (EPA, 1999). Natural VOC emissions from plants are also important. Knowledge of the detailed chemical composition of VOC emissions from major source categories is important because each individual VOC contributes differently to ozone and secondary aerosol formation. VOC emission speciation is therefore an important input to source-oriented photochemical models that are used to help design air pollution control strategies. Exposure to some organic compounds also may pose human health hazards, and consequently compounds such as benzene and 1,3-butadiene have been identified as hazardous air pollutants.

VOC composition profiles also are used in receptor-oriented studies that seek to back-calculate the contributions of various source categories to VOC concentrations observed at ambient air monitoring sites. Accurate VOC profiles for major sources such as motor vehicles are essential to successful application of the chemical mass balance model (Watson, 1984; Lin and Milford, 1994; Fujita et al., 1995; Gertler et al., 1996; Schauer et al., 2002). Many applications of CMB models have focused on understanding sources of VOC with respect to the ozone problem. There is also increasing interest in using these models to expand knowledge regarding the role of different VOC in the formation of secondary organic aerosol (Watson et al., 2001).

The speciation of VOC emitted from motor vehicles reflects the chemical composition of the fuel consumed, with additional species formed and emitted as products of incomplete combustion. These products of incomplete combustion depend on fuel composition (Kaiser et al., 1991; Hoekman, 1992; Leppard et al., 1992; Schuetzle et al., 1994). In addition to tailpipe emissions, VOC emissions from motor vehicles include various categories of evaporative emissions such as resting losses, running losses which occur during vehicle operation due to liquid and vapor leaks in the fuel system, diurnal emissions due to venting of vapors from the fuel tank as ambient temperature rises over the course of the day, and hot soak emissions that occur due to residual engine heat at the end of a trip after the engine has been shut down. Current inventories indicate roughly equal contributions to total VOC emissions from tailpipe and evaporative sources, while other analyses suggest that tailpipe emissions are dominant (Pierson et al., 1999). Some evaporative emissions closely resemble the composition of liquid fuel, in cases such as liquid leaks or liquid fuel spillage during refueling. In other cases, evaporative VOC emissions are heavily enriched in the lightest most volatile compounds present in the liquid fuel, as for example the vapors displaced from a vehicle fuel tank as it is filled with liquid fuel. Haskew et al. (1999) studied running loss evaporative emissions and found that the composition of the emitted VOC was best described as a 50-50 mix of liquid gasoline and headspace vapor compositions.

The speciation of VOC emissions from on-road motor vehicles has been characterized in numerous past studies through measurements in roadway tunnels (Lonneman et al., 1986; Zielinska and Fung, 1994; McLaren et al., 1996; Sagebiel et al., 1996; Fraser et al., 1998; Kirchstetter et al., 1999; Touaty and Bonsang, 2000; Harley et al., 2001). VOC emission speciation also has been reported based on laboratory dynamometer testing of individual vehicles (Sigsby et al., 1987; Hochhauser et al., 1992; Hoekman, 1992; Leppard et al., 1992; Ho and Winer, 1998). The main advantage of laboratory measurements is the ability to control test

conditions including fuel properties, ambient temperature, air conditioner usage, and driving patterns. On-road studies sacrifice some control of test conditions, but benefit from a much larger sample of in-use vehicles than can be tested in the laboratory one vehicle at a time.

Whereas laboratory studies can isolate exhaust via direct sampling of tailpipe emissions, tunnel measurements return a composite of tailpipe and running loss evaporative emissions.

During the 1990s, significant changes were made to California gasoline. In the first phase of California's Reformulated Gasoline (RFG) program, effective in 1992, lead was banned, detergent additives were required, and fuel vapor pressure was reduced. Phase 2 of California's RFG program was implemented in the first half of 1996. Changes to gasoline included increased oxygenate content; reduced contents of sulfur, alkenes, benzene, and other aromatics; reduced vapor pressure, and reductions of mid-point (T_{50}) and heavy-end (T_{90}) distillation temperatures. Most refiners met oxygenate requirements in 1996 through addition of MTBE to gasoline. Since 1996, refiners have exercised the option to develop alternative gasoline formulations with equal emissions-reduction potential according to a predictive model (ARB, 1994). For example, some refiners have reduced their use of oxygenates in gasoline sold in the San Francisco Bay area by making additional reductions in fuel sulfur content and other changes. Due to Federal mandates that apply in areas with serious ozone air pollution problems, use of oxygenates in gasoline is a firm requirement in most of the rest of California including Sacramento and the San Joaquin Valley. In recent years, both MTBE and ethanol have been used as gasoline oxygenates in California. By the end of 2003, blending of MTBE and other ethers in California gasoline had been banned, and refiners switched to ethanol as a fuel oxygenate where one was needed. A summary of the evolution of Bay area gasoline properties since 1994 is provided in Table 1.

The overall objective of the present research is to describe the chemical composition and reactivity of NMOC emissions from motor vehicles during the summer 2000 Central California Ozone Study, and to describe changes that occurred between 1990 and 2000. Separate composition profiles are sought for on-road vehicle emissions, unburned liquid gasoline, and gasoline vapor emissions.

Table 1. Summary of San Francisco Bay area gasoline properties^a (mean $\pm 1\sigma$) during summers 1994-2001.

| gasoline property | 1994 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 |
|---------------------------------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| RVP ^b (kPa) (psi) | 51 ± 1 7.4 ± 0.1 | 51 ± 1 7.4 ± 0.1 | 48 ± 1 7.0 ± 0.1 | 49 ± 1 7.1 ± 0.1 | 48 ± 1 7.0 ± 0.1 | 49 ± 1 7.1 ± 0.1 | 49 ± 1 7.0 ± 0.1 | 49 ± 1 7.0 ± 0.1 |
| sulfur (ppmw) | 131 ± 41 | 81 ± 36 | 16 ± 9 | 12 ± 11 | 16 ± 8 | 10 ± 8 | 9 ± 2 | 10 ± 4 |
| oxygen (wt%) | 0.5 ± 0.3 | 0.2 ± 0.2 | 2.0 ± 0.3 | 1.6 ± 0.6 | 1.6 ± 0.6 | 1.7 ± 0.6 | 1.8 ± 0.3 | 1.5 ± 0.9 |
| MTBE ^c (vol%) | 2.7 ± 1.7 | 1.0 ± 0.9 | 10.7 ± 1.7 | 8.2 ± 3.7 | 7.4 ± 4.3 | 8.0 ± 4.0 | 7.8 ± 4.3 | 5.9 ± 5.6 |
| TAME ^d (vol%) | N/A | N/A | N/A | N/A | 0.5 ± 0.8 | 0.1 ± 0.1 | 0.1 ± 0.8 | 0.2 ± 0.5 |
| ethanol (vol%) | N/A | N/A | N/A | N/A | 0.5 ± 1.6 | 0.7 ± 2.1 | 0.0 ± 0.0 | 0.5 ± 1.3 |
| alkane (vol%) | 57.4 ± 4.8 | 56.6 ± 5.1 | 62.6 ± 2.5 | 65.4 ± 3.7 | 64 ± 3 | 66 ± 5 | 63 ± 5 | 65 ± 4 |
| alkene (vol%) | 7.9 ± 4.4 | 8.8 ± 3.5 | 3.3 ± 0.9 | 3.4 ± 1.2 | 3.6 ± 1.2 | 3.2 ± 2.1 | 4.5 ± 1.8 | 4.3 ± 1.7 |
| aromatic (vol%) | 31.9 ± 2.1 | 33.7 ± 3.3 | 23.5 ± 1.4 | 22.7 ± 1.4 | 24 ± 2 | 22 ± 3 | 25 ± 3 | 24 ± 2 |
| benzene (vol%) | 1.6 ± 0.4 | 1.5 ± 0.4 | 0.4 ± 0.1 | 0.4 ± 0.1 | 0.51 ± 0.08 | 0.52 ± 0.08 | 0.55 ± 0.07 | 0.48 ± 0.06 |
| T ₅₀ (°C) (°F) | 101 ± 4 214 ± 8 | 103 ± 2 218 ± 4 | 93.8 ± 2.2 199 ± 4 | 93.3 ± 1.7 200 ± 3 | 93.3 ± 1.7 200 ± 3 | 93.3 ± 1.1 200 ± 2 | 94.7 ± 2.7 202 ± 5 | 94.4 ± 1.1 202 ± 2 |
| T ₉₀ (°C) (°F) | 168 ± 4 334 ± 8 | 172 ± 4 341 ± 8 | 149 ± 2 300 ± 4 | 148 ± 3 299 ± 6 | 151 ± 4 304 ± 8 | 152 ± 6 306 ± 10 | 151 ± 4 305 ± 7 | 149 ± 2 301 ± 3 |
| density (g L ⁻¹) | 761 ± 8 | 760 ± 4 | 743 ± 2 | 741 ± 5 | 746 ± 5 | 742 ± 6 | 742 ± 6 | 743 ± 7 |

^aSales-weighted average of regular, mid-grade and premium gasoline. Service station samples collected during July in Concord and August in San Francisco, and analyzed by Southwest Research Institute. ^bRVP is Reid Vapor Pressure. ^cMTBE is methyl tertiary butyl ether. ^dTAME is tert-amyl methyl ether.

2. Methods

2.1 Field Sampling

Vehicle emissions were measured in the Caldecott tunnel on highway 24 near Berkeley, California. This tunnel has three bores with two lanes of traffic per bore, on a 4% grade. All tunnel samples reported here were 2-hour averages collected in evacuated stainless steel canisters on summer weekdays from 4-6 PM. In addition to the data of Zielinska and Fung (1994) and Kirchstetter et al. (1999) for 1991 and 1994-97 presented previously, new data from 1999 and 2001 are presented here to permit analysis of emission trends over a 10-year period. Measurements reported here represent emissions from a light-duty gasoline-powered vehicle fleet operating in a warmed-up mode. The number of samples collected each year from 1994 to 2001 varied between 8 and 12.

In 1991, tunnel sampling took place on three afternoons, with 2 co-located samples obtained on two of those days, and a single sample obtained on a third day, for a total of 5 samples (Zielinska and Fung, 1994). Samples in 1991 were collected in bore 1 of the tunnel, in contrast to later measurements which were all obtained in bore 2, where heavy trucks are not allowed. Note that even in bore 1, for 4-6 PM samples, the influence of diesel trucks is minimal because they have relatively low VOC emission factors, and furthermore in the afternoon commuter peak period, heavy trucks represent a small fraction of total traffic.

Tunnel concentrations were generally adjusted to account for background levels of pollutants outside the tunnel. Background concentrations were not measured in 1991, so in effect, zero concentration for all species at the entrance to the tunnel was assumed for the 1991 sampling. For 1994-1997, background concentrations were measured in fresh air that was being injected by ventilation fans into the tunnel. In 1999 and 2001, background measurements were

made at the tunnel entrance with all ventilation fans turned off, allowing a complete mass balance on air flowing through the tunnel. In the past, tunnel concentrations of emitted hydrocarbons were typically much higher than background levels, so differences in handling of background concentrations prior to 1999 are not likely to affect the results reported here.

To determine carbonyl (i.e., aldehyde and ketone) concentrations, additional tunnel and background air samples were collected using dinitrophenylhydrazine (DNPH)-coated silica gel cartridges over 2-h integrated sampling periods from 4 to 6 PM. These samples were co-located with the hydrocarbon canister samples described above.

Liquid gasoline samples were collected at service stations during summer 2001 in Berkeley and Sacramento, California. One liter each of regular and premium grade gasoline was dispensed into separate steel cans for each of 5 major brands in each area. These samples provide a snap-shot of how each refiner chose to meet applicable reformulated gasoline program requirements. Similar samples of liquid gasoline were collected previously in Berkeley during summers 1995, 1996, and 1999.

2.2 Analytical Methods

NMHC concentrations in tunnel canister samples were quantified using gas chromatography with flame ionization detection, following generally similar procedures in all years. Sampling procedures for 1991 and 1994-1997 are presented in detail elsewhere (Zielinska and Fung, 1994; Kirchstetter et al., 1999). In 1991, a modified Chrompack Purge and Trap Injector was used as the cryogenic trapping unit and a 50 m CP-Sil 5 CB capillary column was used for separation. Samples for 1994-1996 were concentrated with a Nutech model 8548 cryogenic concentrator and injected into a Perkin-Elmer model 8500 GC outfitted with a 30 m DB-1 column. For summers 1997, 1999, and 2001, samples were preconcentrated with a Nutech

model 3550A cryogenic concentrator and injected into a Varian CP-3800 gas chromatograph equipped with a DB-1 capillary column. All speciated hydrocarbon analyses of tunnel air samples were conducted by Hesson and coworkers at the Bay Area Air Quality Management District's laboratories in San Francisco, except for the 1991 data of Zielinska and Fung.

After eluting DNPH cartridge samples in acetonitrile, aldehyde and ketone concentrations were quantified using high-performance liquid chromatography (HPLC) using a procedure very similar to that described by Siegl et al. (1992). Carbonyls were quantified by Hoekman and coworkers at Chevron for 1994-96, and by Fung in 1997. In more recent summers (i.e., 1999 and 2001), carbonyl concentrations were determined using a more detailed liquid chromatographic technique with specialized detectors that allowed for quantification of many more carbonyls in the tunnel air samples (Grosjean et al., 1999; Kean et al., 2001).

Detailed liquid gasoline speciation was determined for each gasoline sample by gas chromatography on a Hewlett Packard Model 5890 II GC equipped with dual flame ionization detectors. Primary analysis was performed on a DB-1 capillary column, with co-eluting peaks resolved on a DB-5 column. These analyses were conducted by Kohler and coworkers at ChevronTexaco in Richmond, CA. Typically ~300 species were identified in liquid gasoline samples.

2.3 Headspace Vapor Composition

Headspace vapor composition was estimated in this study from the composition of liquid gasoline using vapor-liquid equilibrium theory, as described previously by Kirchstetter et al. (1999) assuming ideal solution behavior, and by Harley et al. (2000) for non-ideal ethanol-gasoline mixtures. Briefly, measured liquid-phase mol fractions x_i for each species present in

gasoline are multiplied by pure liquid vapor pressures $p_i^{o}(T)$ and activity coefficients γ_i to estimate the partial pressure p_i of each species in the vapor phase (eq 1).

$$p_i = \gamma_i x_i p_i^{\circ}(T) \tag{1}$$

Pure liquid vapor pressures are estimated using the Wagner equation as recommended by Reid et al. (1987). In most cases, we assume γ_i =1 for all species present in liquid fuel (see Harley et al. (2000) for values of γ_i when ethanol is present). Vapor phase mol fractions are computed as y_i = p_i/p_{TOT} , where p_{TOT} is simply the sum of all p_i . Using the molecular weight of each species present in the vapors, it is straightforward to convert from mol fraction y_i to weight fraction w_i in the headspace vapors (eq 2).

$$w_i = \frac{y_i M_i}{\sum_i y_i M_i} \tag{2}$$

The results when expressed in terms of relative composition are not very sensitive to temperature; it is the absolute vapor pressure of gasoline that depends strongly on T, much moreso than the relative composition of the vapors. We use conditions of a hot summer day ($T = 38^{\circ}C = 100^{\circ}F$) in the present analysis.

2.4 Reactivity of Emissions

The maximum incremental reactivity scale (MIR; Carter, 1994) is used to calculate the normalized reactivity of NMOC emissions. MIR is defined under conditions where ozone production is most sensitive to organic gas emissions. Current MIR values based on the SAPRC99 chemical mechanism (Carter, 2002) are combined with NMOC emission profiles that specify the weight fractions w_i of each individual species to determine normalized reactivity R, expressed as the incremental mass of O_3 produced per increment of NMOC mass emitted. As absolute values of R are affected by various modeling assumptions and uncertainties, R is more

meaningful and robust when compared in a relative sense to similar values for other fuels and/or years. The SAPRC99-based MIR values are generally higher than what we have used in previous assessments of VOC reactivity (Kirchstetter et al., 1999).

3. Results and Discussion

3.1 Tunnel NMOC Emissions

Trends in the composition of non-methane organic compound (NMOC) emissions by species class are presented in Figure 1. Effects of California Phase 1 reformulated gasoline use after 1992 are hard to see, whereas the transition to Phase 2 RFG between 1995 and 1996 is readily apparent. Between 1991 and 1994, the n-butane weight fraction in tunnel emissions decreased from $3.4 \pm 0.3\%$ to $2.2 \pm 0.2\%$, consistent with the targeted removal of C_4 hydrocarbons to achieve reductions in gasoline vapor pressure. Starting in 1996, there was a large increase in MTBE emissions (listed as oxygenates in Figure 1), an increase in highly branched alkanes, and a large reduction in aromatics. Isobutene and formaldehyde increased due to increased use of MTBE in gasoline, though the change in isobutene is a small increment compared to ethene and propene that dominate the alkene fraction shown in Figure 1. After 1996 there was a decrease in the mass fractions of both MTBE (5.8 \pm 0.7% in 1996 versus 4.0 \pm 0.5% in 2001) and acetylene (4.9 \pm 0.2% in 1996 versus 2.9 \pm 0.6% in 2001); no other trends are apparent in Figure 1 after 1996. Carbonyl reactivity is dominated by formaldehyde (see Kean et al., 2001); overall carbonyls accounted for ~4 wt% of tunnel NMOC emissions. Note that carbonyl data were not available for 1991.

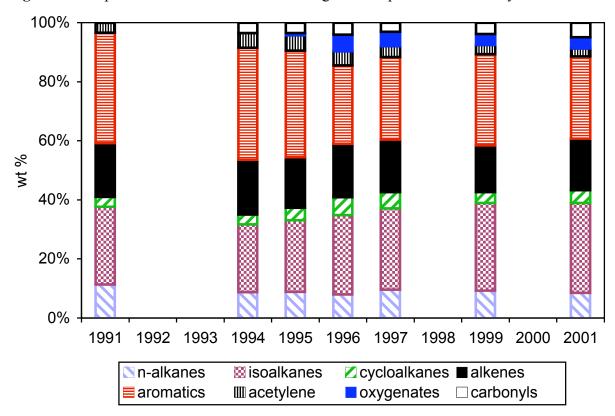


Figure 1. Composition of tunnel non-methane organic compound emissions by class.

Figure 2. Normalized reactivity of tunnel emissions calculated using Carter's MIR scale.

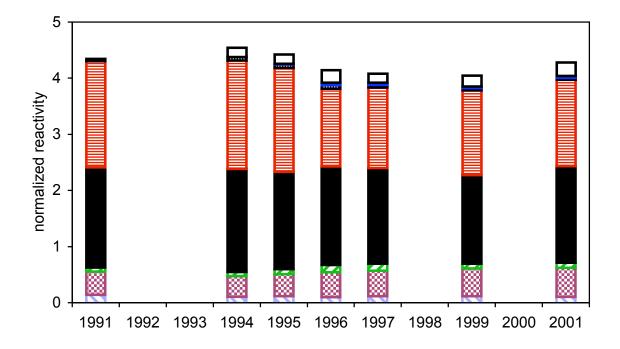


Figure 2 shows that aromatics and alkenes are the dominant contributors to normalized reactivity of tunnel NMOC emissions. Normalized reactivity values are higher than those presented previously for 1994-1997 by Kirchstetter et al. (1999), due to upward revision of MIR values by Carter (2002). In our current assessment, the use of Phase 2 RFG reduced the reactivity of tunnel NMOC emissions by \sim 6%, due primarily to reduced levels of C_9^+ aromatics. This reduction in reactivity is expected to be beneficial in terms of air quality, but is of lesser importance compared to the reduction in NMOC mass emissions that occurred during the 1990s as a combined result of California's low-emission vehicle and reformulated gasoline programs (see Kean et al., 2002).

Figure 3 focuses specifically on aromatic hydrocarbons present in tunnel emissions. The reduction in fuel benzene and total aromatic contents required as part of Phase 2 RFG is clearly apparent in Figure 3, with the benzene weight fraction in tunnel emissions dropping from 6.0 ± 0.3% in 1995 to 3.6-4.2% in 1996 and later years. To reduce the total aromatic content in phase 2 RFG, refiners also targeted C₉ and heavier aromatics. In contrast, C₈ aromatics (xylenes and ethylbenzene) decreased only slightly between 1995 and 1996, and toluene showed no change. Reducing heavy hydrocarbons such as C₉+ aromatics was helpful in achieving a lower T₉₀ distillation temperature (Koehl et al., 1993). In contrast to benzene and monosubstituted aromatics such as toluene and ethylbenzene, the C₉+ aromatics consist mostly of di- and trisubstituted aromatics that are highly reactive. For example, trimethylbenzenes are on average ~4 times more reactive than propylbenzene, which has the same molecular weight (Carter, 2002).

In our 2001 measurements at the Caldecott tunnel, a central research objective was to study the effect of engine load on vehicle emissions. Therefore we measured emissions from 4-6 PM for moderate-load uphill driving on a 4% grade, and also in the morning at the same location

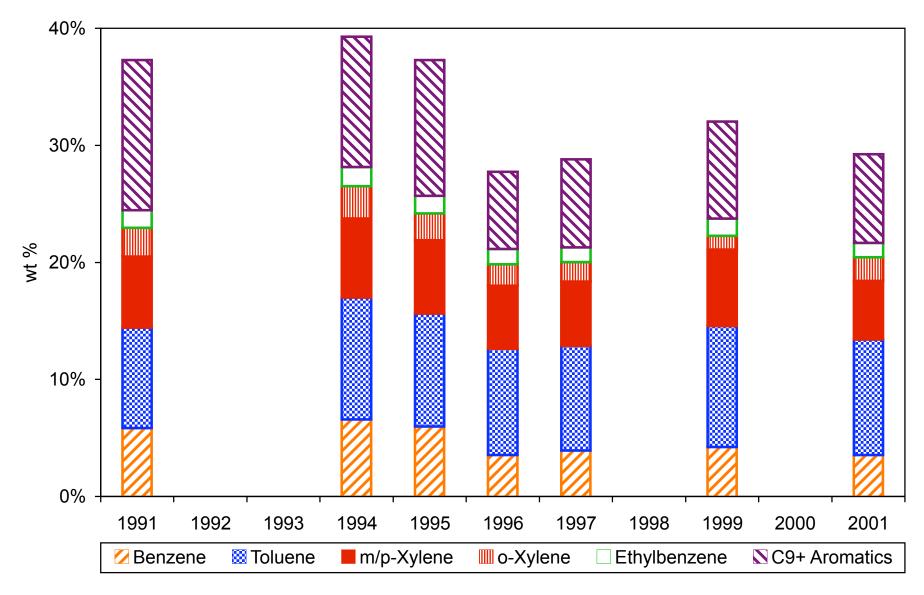


Figure 3. Aromatic hydrocarbons in tunnel emissions, as a fraction of total NMOC. C9+ includes highly reactive aromatics such as ethyltoluene, diethylbenzene, and trimethylbenzene isomers.

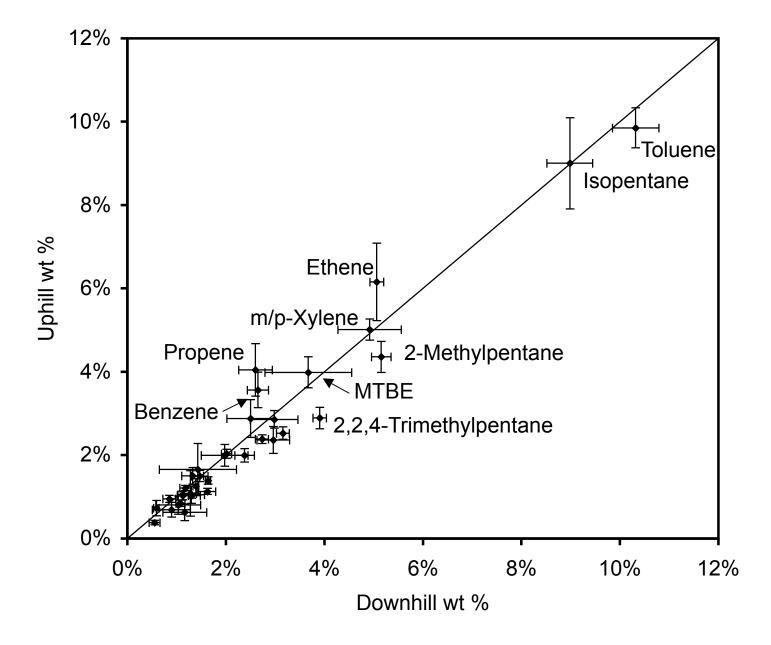


Figure 4. Abundance of individual VOC in tunnel emissions for uphill vs downhill driving during summer 2001.

with downhill driving and much lighter engine load. Interestingly, the absolute concentrations of NMOC at the tunnel exit were almost as high for downhill as for uphill driving, while CO_2 was much higher in uphill driving (see Kean et al., 2003). The relative composition of NMOC emissions for uphill and downhill driving was generally similar, as shown in Figure 4. A regression of individual species weight fractions plotted for uphill vs. downhill driving results in a slope of 0.98 and $R^2 = 0.95$. The vast majority of species fell on or near the 1:1 line (see Figure 4). The relative abundances of ethene, propene, and benzene were higher in uphill driving, consistent with formation of these species as combustion byproducts (Bailey et al., 1990; Ho and Winer, 1998; Kirchstetter et al, 1999). In contrast, unburned fuel species such as 2-methylpentane, 2,2,4-trimethylpentane, and methylcyclopentane, among others, were more abundant in downhill emissions.

3.2 Liquid Gasoline

The measured compositions of liquid gasoline collected in Berkeley (summers 1995, 1996, 1999, and 2001) and Sacramento (summer 2001 only) are summarized in Figure 5. The largest changes in fuel composition occurred between 1995 and 1996: both aromatics and alkenes were reduced in liquid gasoline. Offsetting the decrease in aromatics between 1995 and 1996 were increases in MTBE and isoalkanes, especially highly branched alkanes such as 2,2,4-trimethylpentane (this compound is used to define the 100 octane number rating). The aromatic reduction was also seen in tunnel emissions as shown in Figures 1 and 2 and discussed previously. The reason that reduced alkene content in liquid gasoline did not lead to large changes in alkene emissions is that unburned fuel present in exhaust emissions is augmented by combustion-derived C₂-C₄ alkenes that did not change much as a result of RFG. After 1996, there is a gradual reduction in the use of oxygenates in Bay Area gasoline, which resulted from

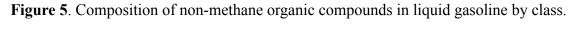
some refiners selling gasoline with little or no oxygenate. In contrast, the Sacramento fuel samples all had at least 2 wt% oxygen in all cases, as required by Federal RFG mandates. Only one brand of gasoline used ethanol as the oxygenate in summer 2001 for both Berkeley and Sacramento. The across the board use of oxygenates in Sacramento led to other differences in fuel composition compared to Berkeley. For example, there was less use of trimethylpentanes and similar compounds in Sacramento gasoline (these are included with isoalkanes in Figure 5). These compounds would not be as much needed in Sacramento gasoline where MTBE and ethanol were used and served as high-octane blending components.

As shown in Figure 6, the normalized reactivity of liquid gasoline decreased by 20-25% as a result of the introduction of Phase 2 RFG. Liquid fuel reactivity is dominated by aromatics, though some additional reduction in reactivity resulted from alkene reductions that occurred between 1995 and 1996. Though Sacramento and Berkeley fuels differ in terms of oxygenate and alkylate use, the reactivity of liquid fuels (dominated by aromatics) is virtually identical.

3.3 Gasoline Headspace Vapors

Gasoline headspace vapors are greatly enriched in the lighter fuel constituents relative to liquid gasoline. Isopentane alone accounts for about a third of headspace vapor mass. n-Butane and n-Pentane are also abundant in headspace vapors, as are oxygenates such as MTBE or ethanol. This short list of compounds (n-butane, n-pentane, isopentane, and MTBE/ethanol) together are responsible for over 60% of headspace vapor mass. As shown in Figure 7, aromatics account for a small fraction of headspace vapor mass (compare with Figure 5 where aromatics are 30% of liquid fuel). The reactivity of headspace vapors shown in Figure 8 shows a reduction of ~20% associated with the introduction of RFG. However in contrast to liquid gasoline where aromatics were the main driver, it was the reduction in light alkenes that led to lower normalized

reactivity of headspace vapors. Just as aromatics and T_{90} distillation temperature specifications interacted to focus efforts on reducing heavy aromatics in gasoline, RVP limits together with alkene specifications may have helped to promote targeted reduction of C_4 - C_5 alkenes that are the most volatile alkenes present in gasoline.



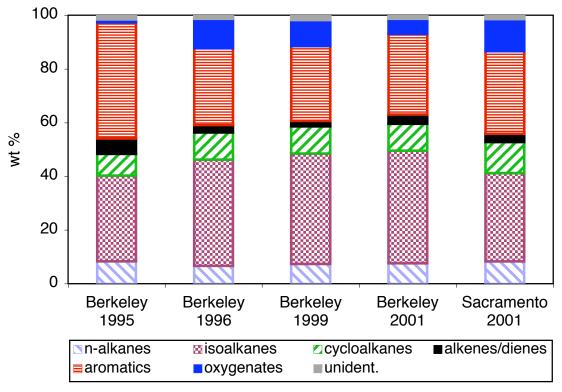
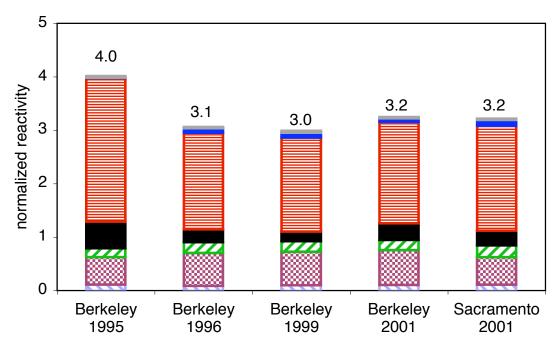
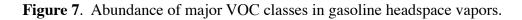


Figure 6. Normalized reactivity of liquid gasoline calculated using Carter's MIR scale.





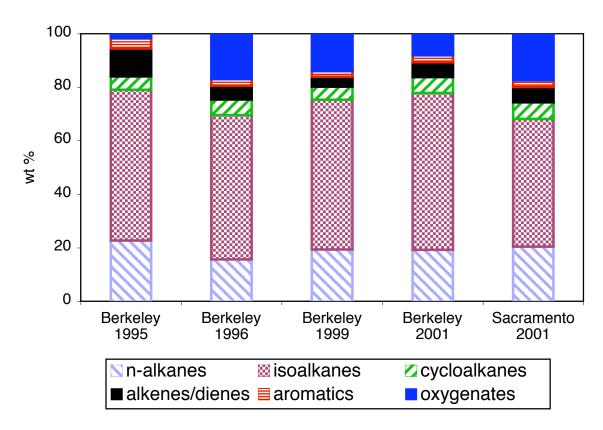
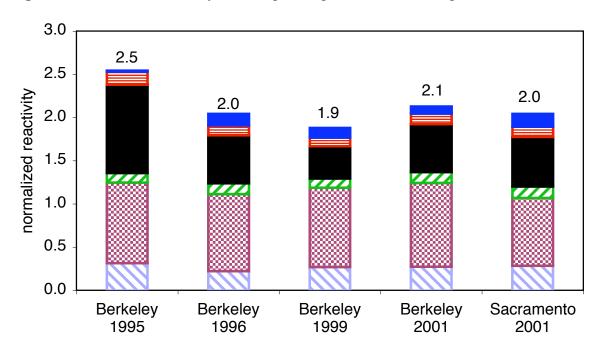


Figure 8. Normalized reactivity of headspace vapors calculated using Carter's MIR scale.



4. Conclusions

The chemical composition of gasoline and of vehicle NMOC emissions changed significantly during the 1990s, mainly as a result of California's reformulated gasoline program. Noteworthy changes include reductions in C₄-C₅ alkenes, benzene, and C₉+ aromatics. At the same time use of trimethylpentanes and oxygenates such as MTBE increased. While the normalized reactivity of liquid gasoline and headspace vapors decreased by ~20%, the reactivity of tunnel emissions decreased by only 6%. The smaller change in reactivity for tunnel emissions is due to the presence in exhaust of reactive alkenes and aldehydes that were absent or only minimally present in unburned fuel.

Between 1996 and 2000, the main change seen in Bay area gasoline was increased use of low- or zero-oxygenate fuel blends by some refiners. Unlike the Bay area, use of oxygenates in gasoline is a firm requirement in the Central Valley of California. Sacramento gasoline samples collected in summer 2001 indicate across the board use of oxygenates in all brands and grades of gasoline. Differences in patterns of oxygenate use between the Bay area and Sacramento led to other fuel differences such as less use of trimethylpentanes in Sacramento gasoline. In summer 2001, only one major brand of gasoline sold in Central California used ethanol as a fuel oxygenate.

5. Recommendations

As California gasoline was reformulated early in 1996, we recommend speciation profiles based on summer 1996 and later data only for use with the summer 2000 Central California Ozone Study. Of the profiles reported here, the summer 1999 and 2001 fuel and tunnel profiles are close matches for the Bay area in summer 2000.

Due to differences in the patterns of oxygenate use in gasoline sold in Central California, different VOC speciation profiles are appropriate for vehicle emissions in the Bay area vs. the Central Valley. Differences are likely to be largest for MTBE and trimethylpentanes. It will be essential to capture regional differences in motor vehicle emission profiles in receptor modeling studies that use those compounds as tracers. Due to its limited use as a fuel oxygenate prior to 2003, ethanol is not appropriate as a tracer for vehicle-related emissions in summer 2000. In photochemical modeling studies, the differences in normalized reactivity of various emission profiles measured since 1996 appear to be small, and could probably be neglected because the mass of VOC emissions has a greater impact on photochemical model O₃ predictions than relatively subtle differences in VOC composition.

To address uncertainties in the relative importance of tailpipe vs. evaporative sources of vehicle emissions, we recommend reconciliation of source profiles presented here with time-resolved ambient VOC concentration measurements made during CCOS.

Literature Cited

ARB (1994). Proposed amendments to the California Phase 2 reformulated gasoline regulations, including amendments for the use of a predictive model. California Air Resources Board, Sacramento, CA.

Bailey, J., Schmidl, B., Williams, M. (1990). Speciated hydrocarbon emissions from vehicles operated over the normal driving speed range on the road. *Atmospheric Environment* **24A**, 43-52.

Carter, W.P.L. (1994). Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air & Waste Management Association* **44**, 881-899.

Carter, W.P.L. (2002). VOC Reactivity Data. http://pah.cert.ucr.edu/~carter/reactdat.htm, accessed November 2002. University of California, Riverside, CA.

EPA (1999). National Air Quality and Emissions Trends Report. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T. (1998). Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environmental Science & Technology*, **32**, 2051-2060.

Fujita, E.M., Watson, J.G., Chow, J.C. (1995). Receptor model and emission inventory source apportionments of nonmethane organic gases in California's San Joaquin Valley and San Francisco Bay Area. *Atmospheric Environment* **29**, 3019-3035.

Gary, J.H., Handwerk, G.E. (2001). Petroleum refining: technology and economics, 4th Edition. Marcel Dekker, New York.

Gertler, A.W., Fujita, E.M., Pierson, W.R., Wittorff, D.N. (1996). Apportionment of NMHC tailpipe and non-tailpipe emissions in the Fort McHenry and Tuscarora Mountain tunnels. *Atmospheric Environment* **30**, 2297-2305.

Gorse, Jr., R.A., Benson, J.D., Burns, V.R., Hochhauser, A.M., Koehl, W.J., Painter, L.J., Reuter, R.M., Rippon, B.H. (1991). Toxic air pollutant vehicle exhaust emissions with reformulated gasolines. *SAE Technical Paper Series* no. 912324.

Grosjean, E.; Green, P.G.; Grosjean, D. (1999). Liquid chromatography analysis of carbonyl (2,4-dinitrophenyl)hydrazones with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry. *Analytical Chemistry* **71**, 1851-1861.

Harley, R.A., Sawyer, R.F., Milford, J.B. (1997). Updated photochemical modeling for California's South Coast Air Basin: Comparison of chemical mechanisms and motor vehicle emission inventories. *Environmental Science & Technology* **31**, 2829-2839.

- Harley, R.A., Coulter-Burke, S.C., Yeung, T.S. (2000). Relating liquid fuel and headspace vapor composition for California reformulated gasoline samples containing ethanol. *Environmental Science & Technology* **34**, 4088-4094.
- Harley, R.A.; McKeen, S.A.; Pearson, J.; Rodgers, M.O.; Lonneman, W.A. (2001). Analysis of motor vehicle emissions during the Nashville/Middle Tennessee Ozone Study. *Journal of Geophysical Research* **106**(D4), 3559-3567.
- Haskew, H.M.; Eng, K.D.; Liberty, T.F.; Reuter, R.M. (1999). Running loss emissions from inuse vehicles. *SAE Technical Paper Series* no. 1999-01-1464.
- Ho, J., Winer, A.M. (1998). Effects of fuel type, driving cycle, and emission status on in-use vehicle exhaust reactivity. *Journal of the Air & Waste Management Association* **48**, 592-603.
- Hochhauser, A.M., Benson, J.D., Burns, V.R., Gorse, Jr., R.A., Koehl, W.J., Painter, L.J., Reuter, R.M., Rutherford, J.A. (1992). Speciation and calculated reactivity of automotive exhaust emissions and their relation to fuel properties. *SAE Technical Paper Series* no. 920325.
- Hoekman, S.K. (1992). Speciated measurements and calculated reactivities of vehicle exhaust emissions from conventional and reformulated gasolines. *Environmental Science & Technology* **26**, 1206-1216.
- IPCC (2001). *Climate Change 2001: The scientific basis*. Intergovernmental Panel on Climate Change, Cambridge University Press, UK.
- Kaiser, E.W., Siegl, W.O., Henig, Y.I., Anderson, R.W., Trinker, F.H. (1991). Effect of fuel structure on emissions from a spark-ignited engine. *Environmental Science & Technology* **25**, 2005-2012,
- Kean, A.J., Grosjean, E., Grosjean, D, Harley, R.A. (2001). On-road measurement of carbonyls in California Light-Duty Vehicle Emissions. *Environmental Science & Technology* **35**, 4198-4204.
- Kean, A.J., Sawyer, R.A., Harley, R.A., Kendall, G.R. (2002). Trends in exhaust emissions from in-use California light-duty vehicles, 1994-2001. *SAE Technical Paper Series* no. 2002-01-1713.
- Kean, A.J.; Harley, R.A.; Kendall, G.R. (2003). Effects of vehicle speed and engine load on motor vehicle emissions. *Environmental Science & Technology* **37**, 3739-3746.
- Kirchstetter, T.W., Singer, B.C., Harley, R.A., Kendall, G.R., Hesson, J.M. (1999). Impact of California reformulated gasoline on motor vehicle emissions. 2. Volatile organic compound speciation and reactivity. *Environmental Science & Technology* **33**, 329-336.
- Koehl, W.J., Benson, J.D., Burns, V.R., Gorse, Jr., R.A., Hochhauser, A.M., Knepper, J.C., Leppard, W.R., Painter, L.J., Rapp, L.A., Reuter, R.M., Rutherford, J.A. (1993). Effects of heavy

- hydrocarbons in gasoline on exhaust mass emissions, air toxics, and calculated reactivity Auto/Oil Air Quality Improvement Program. *SAE Technical Paper Series* No. 932723.
- Leppard, W.R., Rapp, L.A., Burns, V.R., Gorse, R.A., Knepper, J.C., Koehl, W.J. (1992). Effects of gasoline composition on vehicle engine-out and tailpipe hydrocarbon emissions. *SAE Technical Paper Series* no. 920329.
- Leppard, W.R., Benson, J.D., Burns, V.R., Gorse, R.A., Hochhauser, A.M., Knepper, J.C., Koehl, W.J., Rapp, L.A., Reuter, R.M. (1993). How heavy hydrocarbons in the fuel affect exhaust mass emissions: Correlation of fuel, engine-out, and tailpipe speciation. *SAE Technical Paper Series* no. 932725.
- Lin, C., Milford, J.B. (1994). Decay-adjusted chemical mass-balance receptor modeling for volatile organic compounds. *Atmospheric Environment* **28**, 3261-3276.
- Lonneman, W.A.; Seila, R.L.; Meeks, S.A. (1986). Non-methane organic composition in the Lincoln tunnel. *Environmental Science & Technology* **20**, 790-796.
- Marr, L.C., Noblet, G.S., Harley, R.A. (2002). Formation of photochemical air pollution in central California 2. Impact of revised emissions on Eulerian model predictions. *Journal of Geophysical Research Atmospheres* **107**, 4048.
- McLaren, R., Gertler, A.W., Wittorff, D.N., Belzer, W., Dann, T., Singleton, D.L. (1996). Real-world measurements of exhaust and evaporative emissions in the Cassiar Tunnel predicted by chemical mass balance modeling. *Environmental Science and Technology* **30**, 3001-3009.
- NRC (1999). Ozone forming potential of reformulated gasoline. National Academy Press, Washington, D.C.
- Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., Ray, W.D. (1996). Real-world automotive emissions Summary of studies in the Fort McHenry and Tuscarora Mountain Tunnels. *Atmospheric Environment* **30**, 2233-2256.
- Pierson, W.R., Schorran, D.E., Fujita, E.M., Sagebiel, J.C., Lawson, D.R., Tanner, R.L. (1999). Assessment of nontailpipe hydrocarbon emissions from motor vehicles. *Journal of the Air & Waste Management Assocation* **49**, 498-519.
- Reid, R.C.; Prausnitz, J.M.; Poling, B.E. (1987). *The Properties of Gases & Liquids*, 4th edition. McGraw-Hill, New York, NY. See p. 212 and Appendix A.
- Reuter, R.M., Gorse, R.A., Jr., Painter, L.J., Benson, J.D., Hochhauser, A.M., Rippon, B.H., Burns, V.R., Koehl, W.J.; Rutherford, J.A. (1992). Effects of oxygenated fuels and RVP on automotive emissions. *SAE Technical Paper Series* no. 920326.

- Sagebiel, J.C., Zielinska, B., Pierson, W.R., Gertler, A.W. (1996). Real-world emission and calculated reactivities of organic species from motor vehicles. *Atmospheric Environment* **30**, 2287-2296.
- Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T. (2002). Source reconciliation of atmospheric gas-phase and particle phase-pollutants during a severe photochemical smog episode. *Environmental Science and Technology* **36**, 3806-3814.
- Schuetzle, D., Siegl, W.O., Jenson, T.E., Dearth, M.A., Kaiser, E.W., Gorse, R., Kreucher, W., Kulik, E. (1994). The relationship between gasoline composition and vehicle hydrocarbon emissions: A review of current studies and future research needs. *Environmental Health Perspectives* **102**, Supplement 4.
- Seinfeld, J.H., Pandis, S.N. (1997). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley-Interscience, New York.
- Sigsby, J.E.; Tejada, S.; Ray, W.; Lang, J.M.; Duncan, J.W. (1987). Volatile organic compound emissions from 46 in-use passenger cars. *Environmental Science & Technology* **21**, 466-475.
- Touaty, M., Bonsang, B. (2000). Hydrocarbon emissions in a highway tunnel in the Paris area. *Atmospheric Environment* **34**, 985-996.
- Watson, J.G. (1984). Overview of receptor model principles. *Journal of the Air Pollution Control Association* **27**, 98-104.
- Watson, J.G., Chow, J.C., Fujita, E.M. (2001). Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment* **35**, 1567-1584.
- Zielinska, B., Fung, K.K. (1994). The composition and concentration of hydrocarbons in the range of C_2 to C_{18} emitted from motor vehicles. *The Science of the Total Environment* **146/147**, 281-288.

Appendix

The following pages provide detailed tabulations of the mass fractions of individual organic compounds in tunnel emissions, liquid gasoline, and headspace vapors.

| wt% in Tunnel Emissions | Caldecot | t 1999 | Caldecot | Caldecott 2001 | | |
|----------------------------|----------------|----------------|----------------|----------------|--|--|
| Species | NMOC wt% | st dev | NMOC wt% | st dev | | |
| | | | | | | |
| n-alkanes | | | | | | |
| ethane | 0.88% | 0.47% | 1.03% | 0.71% | | |
| propane | 0.19% | 0.12% | 0.17% | 0.09% | | |
| butane | 1.68% | 0.14% | 1.43% | 0.26% | | |
| pentane | 2.85% | 0.16% | 2.72% | 0.27% | | |
| hexane | 1.45% | 0.06% | 1.32% | 0.12% | | |
| heptane | 0.98% | 0.06% | 0.80% | 0.10% | | |
| octane | 1.01% | 0.10% | 0.30% | 0.05% | | |
| nonane | 0.17% | 0.05% | 0.25% | 0.09% | | |
| decane | | | 0.24% | 0.19% | | |
| undecane | 0.05% | 0.05% | 0.22% | 0.11% | | |
| dodecane | 0.03% | 0.03% | 0.06% | 0.08% | | |
| | | | | | | |
| isoalkanes | | | | | | |
| Isobutane | 0.22% | 0.04% | 0.29% | 0.07% | | |
| Isopentane | 10.72% | 0.54% | 8.55% | 1.42% | | |
| 2,2 Dimethylbutane | 1.56% | 0.14% | 0.90% | 0.11% | | |
| 2-Methylpentane | 3.04% | 0.14% | 4.14% | 0.48% | | |
| 3 Methylpentane | 2.43% | 0.09% | 2.26% | 0.13% | | |
| 2,3 Dimethylpentane | 0.54% | 0.05% | 1.19% | 0.24% | | |
| 2 Methylhexane | 0.59% | 0.08% | 1.89% | 0.21% | | |
| 3 Methylhexane | 1.34% | 0.08% | 2.25% | 0.42% | | |
| 2,2,4 Trimethylpentane | 3.54% | 0.15% | 2.75% | 0.34% | | |
| 2,3,4 Trimethylpentane | 1.58% | 0.10% | 1.07% | 0.09% | | |
| 2,3 Dimethylhexane | 0.51% | 0.09% | 0.29% | 0.29% | | |
| 2,5 Dimethylhexane | 0.31% | 0.06% | 0.65% | 0.23% | | |
| 2 Methylheptane | 0.23% | 0.03% | 0.39% | 0.02% | | |
| 3 Methylheptane | 0.50% | 0.29% | 0.36% | 0.07% | | |
| Other isoalkanes | 1.97% | | 2.42% | | | |
| | | | | | | |
| cycloalkanes (naphthenes) | | | | | | |
| Cyclopentane/2,3-dm-butane | 0.52% | 0.34% | 0.76% | 0.28% | | |
| Cyclohexane | 0.52% | 0.16% | 0.98% | 0.08% | | |
| Methylcyclopentane | 2.54% | 0.09% | 2.40% | 0.20% | | |
| Methylcyclohexane | 0.67% | 0.15% | 0.98% | 0.13% | | |
| | | | | | | |
| alkenes (olefins) | | | | | | |
| Ethene | 6.89% | 1.06% | 5.85% | 1.21% | | |
| Propene | 4.30% | 0.60% | 3.84% | 0.82% | | |
| Isobutene/1 Butene | 1.53% | 1.19% | 1.58% | 0.80% | | |
| Cis-2-butene | 0.31% | 0.16% | 0.38% | 0.16% | | |
| Trans-2-butene | 0.28% | 0.05% | 0.34% | 0.05% | | |
| 1,3 Butadiene | 0.71% | 0.11% | 0.48% | 0.32% | | |
| 1-Pentene | 0.16% | 0.07% | 0.21% | 0.05% | | |
| 3 Methyl-1-butene | 0.13% | 0.02% | 0.10% | 0.08% | | |
| 2-Methyl-1 butene | 0.02% | 0.04% | 0.22% | 0.16% | | |
| 1-Pentene | 0.16% 0.13% | 0.07% 0.02% | 0.21% 0.10% | 0.05% 0.08% | | |

| wt% in Tunnel Emissions | Caldecot | t 1999 | Caldecot | t 2001 |
|-------------------------|----------|--------|----------|--------|
| Species | NMOC wt% | st dev | NMOC wt% | st dev |
| | | | | |
| 2-Methyl-2-butene | 0.01% | 0.02% | 0.34% | 0.17% |
| Cis-2-pentene | 0.14% | 0.07% | 0.16% | 0.02% |
| Trans-2-pentene | 0.20% | 0.08% | 0.25% | 0.05% |
| 1-Hexene | 0.13% | 0.03% | 0.16% | 0.10% |
| 4-Methyl-1-pentene | 0.02% | 0.03% | 0.10% | 0.11% |
| 2 Methyl-1-pentene | 0.00% | 0.00% | 0.09% | 0.21% |
| Other alkenes | 0.95% | | 3.32% | |
| | | | | |
| aromatics | | | | |
| Benzene | 4.07% | 0.22% | 3.38% | 0.55% |
| Toluene | 9.93% | 0.54% | 9.36% | 0.62% |
| Styrene | 0.30% | 0.04% | 0.39% | 0.21% |
| Ethylbenzene | 1.42% | 0.05% | 1.15% | 0.08% |
| o-Xylene | 1.14% | 0.25% | 1.93% | 0.14% |
| m/p Xylene | 6.27% | 0.26% | 4.76% | 0.33% |
| Cumene | 0.10% | 0.04% | 0.12% | 0.05% |
| n-propylbenzene | 0.26% | 0.06% | 0.23% | 0.09% |
| m-Ethyltoluene | 0.76% | 0.16% | 1.90% | 0.34% |
| p-Ethyltoluene | 0.45% | 0.28% | 0.24% | 0.28% |
| o-Ethyltoluene | 0.16% | 0.11% | 0.37% | 0.30% |
| 1,2,3 Trimethylbenzene | 0.63% | 0.11% | 0.62% | 0.54% |
| 1,2,4 Trimethylbenzene | 2.41% | 0.61% | 1.43% | 0.17% |
| 1,3,5 Trimethylbenzene | 0.55% | 0.36% | 0.69% | 0.24% |
| Sec-butylbenzene | 0.33% | 0.07% | 0.02% | 0.05% |
| n-butylbenzene | 0.62% | 0.18% | 0.30% | 0.20% |
| Other C10+ Aromatics | 1.38% | | 0.89% | |
| | | | | |
| other | | | | |
| Ethyne (Acetylene) | 3.16% | 0.35% | 2.74% | 0.59% |
| MTBE | 3.74% | 0.26% | 3.79% | 0.48% |
| | | | | |
| carbonyls | | | | |
| formaldehyde | 1.755% | 0.263% | 2.379% | 0.210% |
| acetaldehyde | 0.468% | 0.056% | 0.512% | 0.048% |
| propanal | 0.047% | 0.006% | 0.067% | 0.006% |
| butanal | 0.033% | 0.009% | 0.044% | 0.003% |
| pentanal | 0.020% | 0.008% | 0.027% | 0.003% |
| isopentanal | 0.019% | 0.012% | 0.033% | 0.003% |
| hexanal | 0.012% | 0.008% | 0.021% | 0.003% |
| heptanal | 0.006% | 0.003% | 0.013% | 0.002% |
| acrolein | 0.059% | 0.006% | 0.129% | 0.013% |
| methacrolein | 0.094% | 0.011% | 0.100% | 0.007% |
| crotonaldehyde | 0.062% | 0.009% | 0.058% | 0.005% |
| 3-pentene-2-one | 0.009% | 0.003% | | |
| benzaldehyde | 0.281% | 0.045% | 0.343% | 0.031% |
| o-tolualdehyde | 0.086% | 0.011% | 0.108% | 0.005% |
| | | | | |

| OC wt% | st dev N | IMOC wt% | st dev |
|--------|--|---|---|
| | | | |
| | | | |
| 199% | 0.239% | 0.268% | 0.028% |
| 109% | 0.016% | 0.151% | 0.016% |
| 070% | 0.009% | 0.104% | 0.009% |
| 047% | 0.006% | 0.060% | 0.005% |
| 024% | 0.002% | 0.025% | 0.002% |
| 021% | 0.005% | | |
| 005% | 0.001% | 0.009% | 0.002% |
| 230% | 0.032% | 0.370% | 0.010% |
| 032% | 0.005% | 0.049% | 0.004% |
| 023% | 0.016% | 0.034% | 0.006% |
| 028% | 0.013% | 0.026% | 0.003% |
| 005% | 0.002% | 0.009% | 0.002% |
| 043% | 0.010% | 0.050% | 0.006% |
| 007% | 0.002% | 0.008% | 0.002% |
| 002% | 0.001% | 0.005% | 0.001% |
| | 199% 109% 070% 047% 024% 021% 005% 230% 023% 023% 005% 043% 007% | 109% 0.016% 070% 0.009% 047% 0.006% 024% 0.002% 021% 0.005% 005% 0.001% 230% 0.032% 023% 0.016% 028% 0.013% 005% 0.002% 043% 0.010% 007% 0.002% | 109% 0.016% 0.151% 070% 0.009% 0.104% 047% 0.006% 0.060% 024% 0.002% 0.025% 021% 0.005% 0.009% 230% 0.032% 0.370% 023% 0.016% 0.049% 023% 0.016% 0.034% 028% 0.013% 0.026% 005% 0.002% 0.009% 043% 0.010% 0.050% 007% 0.002% 0.008% |

| wt% in Liquid Gasoline Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|--------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| n-alkanes | | | | | |
| Propane | 0.0283 | 0.0076 | 0.0126 | 0.0103 | 0.0183 |
| Butane | 1.0099 | 0.6300 | 0.9723 | 0.7871 | 0.8893 |
| Pentane | 3.1572 | 2.4246 | 2.3479 | 2.8888 | 2.8296 |
| Hexane | 1.9974 | 1.5031 | 1.3979 | 1.7116 | 1.9026 |
| Heptane | 1.3789 | 1.2453 | 1.4922 | 1.4562 | 1.6101 |
| Octane | 0.4683 | 0.5173 | 0.6515 | 0.4724 | 0.6452 |
| Nonane | 0.1570 | 0.2007 | 0.3296 | 0.1859 | 0.2801 |
| Decane | 0.0551 | 0.0399 | 0.0776 | 0.0766 | 0.1191 |
| Hendecane | 0.0448 | 0.0307 | 0.0627 | 0.0473 | 0.0541 |
| Dodecane | 0.0213 | 0.0097 | 0.0119 | 0.0116 | 0.0179 |
| Tridecane | 0.0088 | 0.0044 | 0.0044 | 0.0000 | 0.0000 |
| Tetradecane | 0.0029 | 0.0000 | 0.0011 | 0.0000 | 0.0000 |
| Pentadecane | 0.0061 | 0.0027 | 0.0052 | 0.0000 | 0.0000 |
| isoalkanes | | | | | |
| 2-methylpropane | 0.2382 | 0.0935 | 0.0886 | 0.0660 | 0.1737 |
| 2-methylbutane | 9.4849 | 8.8111 | 8.9207 | 9.3192 | 7.5069 |
| 2,2-dimethylpropane | 0.0109 | 0.0137 | 0.0186 | 0.0054 | 0.0078 |
| 2-methylpentane | 4.4643 | 4.2655 | 4.0664 | 4.5749 | 3.5513 |
| 3-methylpentane | 2.8354 | 2.6060 | 2.4876 | 2.7622 | 2.1913 |
| 2,2-dimethylbutane | 0.9596 | 0.8159 | 1.2452 | 1.3265 | 0.9615 |
| 2,3-dimethylbutane | 1.0921 | 1.3624 | 1.5084 | 1.6169 | 1.1369 |
| 2-methylhexane | 1.8286 | 1.5372 | 1.3902 | 1.5340 | 1.4939 |
| 3-methylhexane | 2.0119 | 1.8010 | 1.7750 | 1.9432 | 1.8991 |
| 3-ethylpentane | 0.1714 | 0.1058 | 0.0802 | 0.0748 | 0.1326 |
| 2,2-dimethylpentane | 0.1512 | 0.0938 | 0.1003 | 0.1141 | 0.1147 |
| 2,3-dimethylpentane | 0.9950 | 1.4178 | 1.6668 | 2.0713 | 1.7083 |
| 2,4-dimethylpentane | 0.5121 | 0.7625 | 0.8777 | 0.9339 | 0.7323 |
| 33-Dimethylpentane | 0.1462 | 0.1135 | 0.0000 | 0.1123 | 0.1132 |
| 223-Trimethylbutane | 0.0000 | 0.0418 | 0.0000 | 0.0463 | 0.0362 |
| 2-Methylheptane | 0.6309 | 0.7821 | 0.8162 | 0.7197 | 0.8474 |
| 3-methylheptane | 0.7882 | 0.8442 | 0.8276 | 0.7614 | 0.8389 |
| 4-Methylheptane | 0.3221 | 0.3853 | 0.3806 | 0.3463 | 0.3798 |
| 2,2-dimethylhexane | 0.0643 | 0.0465 | 0.0493 | 0.0493 | 0.0481 |
| 2,4-dimethylhexane | 0.3332 | 0.5962 | 0.6593 | 0.5834 | 0.4218 |
| 2,5-dimethylhexane | 0.2767 | 0.5786 | 0.6862 | 0.5719 | 0.3805 |
| 3,3-dimethylhexane | 0.0654 | 0.0509 | 0.0508 | 0.0535 | 0.0554 |
| 2-Me-3-Et-pentane | 0.3160 | 0.5834 | 0.6658 | 0.6099 | 0.4214 |
| 2,4-dimethylheptane | 0.0813 | 0.2388 | 0.0917 | 0.0728 | 0.0568 |
| 2,6-dimethylheptane | 0.0734 | 0.1778 | 0.2117 | 0.1351 | 0.2164 |
| 2,5-dimethylheptane | 0.0089 | 0.0099 | 0.0061 | 0.0128 | 0.0044 |
| 3,5-dimethylheptane | 0.2148 | 0.3556 | 0.3461 | 0.2747 | 0.3080 |
| 2,3-dimethylheptane | 0.0668 | 0.1161 | 0.1126 | 0.1086 | 0.1022 |
| 3,4-dimethylheptane | 0.0350 | 0.0726 | 0.0695 | 0.0594 | 0.0662 |
| 3,3-dimethylheptane | 0.0266 | 0.0420 | 0.0479 | 0.0241 | 0.0381 |
| -,- aa,opta | 5.5200 | 5.5.20 | 0.0.75 | J.J. | 0.0001 |

| wt% in Liquid Gasoline Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|--------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| 4,4-dimethylheptane | 0.0031 | 0.0339 | 0.0285 | 0.0173 | 0.0248 |
| 2-methyloctane | 0.1955 | 0.2788 | 0.2784 | 0.2271 | 0.2767 |
| 3-methyloctane | 0.2217 | 0.3214 | 0.3443 | 0.2976 | 0.3480 |
| 4-methyloctane | 0.1647 | 0.2304 | 0.2337 | 0.1882 | 0.2333 |
| 3-ethylheptane | 0.0592 | 0.0901 | 0.0984 | 0.0644 | 0.0919 |
| 4-ethylheptane | 0.0393 | 0.0459 | 0.0433 | 0.0387 | 0.0467 |
| 2,2-dimethylheptane | 0.0197 | 0.0151 | 0.0159 | 0.0165 | 0.0181 |
| 3-Me-4-Et-hexane | 0.0181 | 0.0086 | 0.0137 | 0.0135 | 0.0070 |
| 2-methylnonane | 0.0760 | 0.0851 | 0.1196 | 0.0876 | 0.1153 |
| 3-methylnonane | 0.0756 | 0.0749 | 0.1134 | 0.0833 | 0.1096 |
| 4-methylnonane | 0.0992 | 0.2251 | 0.2963 | 0.2612 | 0.2310 |
| 3-ethyloctane | 0.0000 | 0.0000 | 0.0076 | 0.0000 | 0.0000 |
| 4-ethyloctane | 0.0318 | 0.0453 | 0.0648 | 0.0356 | 0.0461 |
| 2,2-dimethyloctane | 0.0301 | 0.0489 | 0.0179 | 0.0241 | 0.0454 |
| 2,3-dimethyloctane | 0.0220 | 0.0233 | 0.0443 | 0.0243 | 0.0370 |
| 2,6-dimethyloctane | 0.0000 | 0.0207 | 0.0336 | 0.0012 | 0.0210 |
| 4,4-dimethyloctane | 0.0150 | 0.0199 | 0.0269 | 0.0147 | 0.0219 |
| 2-methyldecane | 0.0098 | 0.0659 | 0.0764 | 0.0760 | 0.0200 |
| 3-methyldecane | 0.0339 | 0.0182 | 0.0368 | 0.0277 | 0.0315 |
| 2,6-dimethylnonane | 0.0166 | 0.0118 | 0.0495 | 0.0185 | 0.0336 |
| C-11 Isoparaffins | 0.0087 | 0.0095 | 0.0073 | 0.0120 | 0.0119 |
| C-10 Isoparaffin O | 0.0025 | 0.0201 | 0.0282 | 0.0181 | 0.0189 |
| 2-Me-3-Et-heptane | 0.0285 | 0.0538 | 0.0389 | 0.0157 | 0.0473 |
| 2,6-diMe-hendecane | 0.0167 | 0.0050 | 0.0091 | 0.0053 | 0.0063 |
| 223-triMe-pentane | 0.0696 | 0.1984 | 0.2440 | 0.2049 | 0.1140 |
| 224-triMe-pentane | 0.9059 | 3.6395 | 4.0649 | 3.7172 | 1.9274 |
| 233-triMe-pentane | 0.4868 | 1.6723 | 2.0808 | 1.8074 | 0.9690 |
| 234-triMe-pentane | 0.4324 | 1.6537 | 1.9736 | 1.7771 | 0.9494 |
| 225-trimethylhexane | 0.1646 | 0.9648 | 0.5969 | 1.0697 | 0.3790 |
| 235-trimethylhexane | 0.0671 | 0.2042 | 0.1268 | 0.2281 | 0.0961 |
| 244-trimethylhexane | 0.0970 | 0.0850 | 0.0628 | 0.0816 | 0.0808 |
| 223-trimethylhexane | 0.0237 | 0.0077 | 0.0073 | 0.0271 | 0.0336 |
| C-11 Isoparaf alky | 0.0101 | 0.0239 | 0.0336 | 0.0137 | 0.0274 |
| 223-triMethylheptane | 0.0413 | 0.0573 | 0.0716 | 0.0468 | 0.0606 |
| 244-triMe-heptane | 0.0000 | 0.1616 | 0.0000 | 0.0256 | 0.0359 |
| 224-triMe-heptane | 0.0136 | 0.0325 | 0.0315 | 0.0326 | 0.0200 |
| 225-triMe-heptane | 0.0237 | 0.0486 | 0.0501 | 0.0328 | 0.0518 |
| 335-triMe-heptane | 0.0033 | 0.0000 | 0.0006 | 0.0012 | 0.0002 |
| 236-triMe-heptane | 0.0195 | 0.0492 | 0.0553 | 0.0537 | 0.0410 |
| 245-triMe-heptane | 0.0179 | 0.0205 | 0.0238 | 0.0189 | 0.0201 |
| 246-triMe-heptane | 0.0168 | 0.0173 | 0.0142 | 0.0187 | 0.0166 |
| 255-triMe-heptane | 0.0312 | 0.0783 | 0.0829 | 0.0828 | 0.0657 |
| C-11 Isoparaf Alky B | 0.0085 | 0.0059 | 0.0184 | 0.0072 | 0.0111 |
| C-11 Isoparaf Alky C | 0.0154 | 0.1023 | 0.1375 | 0.1119 | 0.0646 |
| C-11 Isoparaf Alky D | 0.0172 | 0.0138 | 0.0724 | 0.0324 | 0.0294 |
| C-11 Isoparaf Alky E | 0.0160 | 0.0433 | 0.0483 | 0.0197 | 0.0193 |

| wt% in Liquid Gasoline Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|--|------------------|------------------|------------------|------------------|--------------------|
| C-11 Isoparaf Alky F C-12 isoparaf Alky A | 0.0000 0.0154 | 0.0179 0.0232 | 0.0259 0.0182 | 0.0069 0.0206 | 0.0092 0.0073 |
| C-12 isoparaf Alky B | 0.0045 | 0.0006 | 0.0013 | 0.0005 | 0.0000 |
| 2,6,10triM-hendecane | 0.0085 | 0.0055 | 0.0050 | 0.0048 | 0.0044 |
| 2,6,10triMe-dodecane | 0.0188 | 0.0033 | 0.0139 | 0.0042 | 0.0026 |
| cycloalkanes (naphthenes) | | | | | |
| C-9 Naphthenes | 0.0390 | 0.0125 | 0.0327 | 0.0384 | 0.0428 |
| Cyclopentane | 0.5598 | 0.5146 | 0.4650 | 0.5096 | 0.5164 |
| Methylcyclopentane | 2.5766 | 3.0458 | 2.1473 | 2.7458 | 2.7609 |
| Ethylcyclopentane | 0.1761 | 0.2659 | 0.2608 | 0.2468 | 0.3601 |
| 1,1-diMecyclopentane | 0.0130 | 0.0042 | 0.0008 | 0.0011 | 0.0023 |
| 1T2-diMecyclopentane | 0.4429 | 0.4071 | 0.4655 | 0.4789 | 0.6252 |
| 1C3-diMecyclopentane | 0.5602 | 0.5156 | 0.5039 | 0.5523 | 0.6786 |
| 1T3-diMecyclopentane | 0.4662 | 0.4273 | 0.4325 | 0.4697 | 0.5777 |
| Propylcyclopentane | 0.0102 | 0.0222 | 0.0224 | 0.0174 | 0.0214 |
| 112-triMeCyPentane | 0.0161 | 0.0058 | 0.0024 | 0.0142 | 0.0058 |
| 113-triMeCyPentane | 0.0717 | 0.1037 | 0.1050 | 0.0937 | 0.1354 |
| 1C2C3-triMeCypentane | 0.0091 | 0.0034 | 0.0020 | 0.0035 | 0.0034 |
| 1C2T3-triMeCyPentane | 0.0204 | 0.0111 | 0.0095 | 0.0110 | 0.0114 |
| 1T2C3-triMeCyPentane | 0.0539 | 0.1076 | 0.1304 | 0.0856 | 0.1444 |
| 1C2C4-triMeCyPentane | 0.0120 | 0.0042 | 0.0025 | 0.0038 | 0.0034 |
| 1T2C4-triMeCyPentane | 0.0984 | 0.1967 | 0.2175 | 0.1432 | 0.2196 |
| 113-t4-tetraMeCyPent | 0.0524 | 0.1023 | 0.2697 | 0.0681 | 0.1097 |
| 1Me-1EtCyclopentane | 0.0449 | 0.0861 | 0.1045 | 0.0553 | 0.1186 |
| 1Me-C2EtCyclopentane | 0.0282 | 0.0545 | 0.0482 | 0.0365 | 0.0602 |
| 1MeC3EtCyclopentane | 0.0701 | 0.1601 | 0.1595 | 0.1055 | 0.1652 |
| 1-M-t-3-Et Cycpentane | 0.0922 | 0.1479 | 0.1494 | 0.1058 | 0.1454 |
| C-9 Naphthene A | 0.0336 | 0.0117 | 0.0083 | 0.0130 | 0.0125 |
| C-9 Naphthene B | 0.0111 | 0.0094 | 0.0098 | 0.0087 | 0.0113 |
| C-9 Naphthene I | 0.0233 | 0.0067 | 0.0098 | 0.0192 | 0.0098 |
| Cyclohexane | 0.9125 | 1.4150 | 1.1131 | 1.6740 | 1.6121 |
| Methylcyclohexane | 1.0587 | 1.2251 | 1.5061 | 1.4362 | 1.7756 |
| Ethylcyclohexane | 0.0404 | 0.1003 | 0.2623 | 0.1212 | 0.2144 |
| 1,1-diMecyclohexane | 0.0187 | 0.0281 | 0.0321 | 0.0235 | 0.0325 |
| 1C2-diMecyclohexane | 0.0357 | 0.0700 | 0.0690 | 0.0391 | 0.0607 |
| 1T2-diMecyclohexane | 0.0505 | 0.1314 | 0.1376 | 0.0847 | 0.1148 |
| 1C3-diMecyclohexane | 0.0983 | 0.2786 | 0.3225 | 0.1703 | 0.2563 |
| 1T3-diMecyclohexane | 0.0930 | 0.2265 | 0.1413 | 0.1346 | 0.1849 |
| 1C4-diMecyclohexane | 0.0400 | 0.0096 | 0.1275 | 0.0304 | 0.0579 |
| Propylcyclohexane | 0.0208 | 0.0451 | 0.0702 | 0.0291 | 0.0484 |
| iso-Bu-Cyclohexane | 0.0050 | 0.0032 | 0.0043 | 0.0040 | 0.0040 |
| sec-Bu-Cyclohexane | 0.0124 | 0.0094 | 0.0302 | 0.0129 | 0.0162 |
| 1MeC3Etcyclohexane | 0.0699 | 0.0458 | 0.2527 | 0.1264 | 0.1519 |
| 1MeC4EtCyclohexane | 0.0195 | 0.0113 | 0.0120 | 0.0074 | 0.0115 |
| 1MeT4Etcyclohexane | 0.0174 | 0.0305 | 0.0354 | 0.0209 | 0.0328 |

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|--------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| 113-triMecyclohexane | 0.0266 | 0.0494 | 0.0489 | 0.0312 | 0.0439 |
| 1C2C3-triMeCyhexane | 0.0080 | 0.0000 | 0.0003 | 0.0000 | 0.0000 |
| 1C2T3-triMeCyhexane | 0.0481 | 0.0296 | 0.0278 | 0.0218 | 0.0252 |
| 1C3T5-triMeCyhexane | 0.0491 | 0.1665 | 0.1893 | 0.0924 | 0.1258 |
| 1-M-t2-PropCyHexane | 0.0296 | 0.0494 | 0.0618 | 0.0561 | 0.0470 |
| C-10 Cyclohexane AA | 0.0051 | 0.0127 | 0.0294 | 0.0112 | 0.0173 |
| C-10 Cyclohexane BB | 0.0111 | 0.0167 | 0.0452 | 0.0174 | 0.0304 |
| 2MePropylCyclohexane | 0.0000 | 0.0000 | 0.0523 | 0.0129 | 0.0057 |
| Cis-hydrindane | 0.0104 | 0.0143 | 0.0130 | 0.0102 | 0.0149 |
| alkenes (olefins) | | | | | |
| Propene | 0.0106 | 0.0000 | 0.0003 | 0.0022 | 0.0008 |
| 1-butene | 0.0194 | 0.0102 | 0.0075 | 0.0042 | 0.0077 |
| Cis-2-butene | 0.0465 | 0.0385 | 0.0278 | 0.0156 | 0.0244 |
| Trans-2-butene | 0.0419 | 0.0607 | 0.0375 | 0.0267 | 0.0286 |
| 2-methylpropene | 0.0220 | 0.0127 | 0.0058 | 0.0045 | 0.0118 |
| 1-pentene | 0.2293 | 0.0585 | 0.0433 | 0.0469 | 0.1051 |
| Cis-2-pentene | 0.2574 | 0.1037 | 0.0794 | 0.0975 | 0.1267 |
| trans-2-pentene | 0.4604 | 0.2459 | 0.1799 | 0.2192 | 0.2560 |
| 2-methyl-1-butene | 0.3289 | 0.1158 | 0.0511 | 0.1097 | 0.1745 |
| 3-methyl-1-butene | 0.0684 | 0.0165 | 0.0217 | 0.0146 | 0.0308 |
| 2-methyl-2-butene | 0.6411 | 0.3689 | 0.1405 | 0.3979 | 0.4083 |
| 1-hexene | 0.1049 | 0.0248 | 0.0237 | 0.0346 | 0.0388 |
| Cis-2-hexene | 0.1127 | 0.0397 | 0.0460 | 0.0842 | 0.0506 |
| Trans-2-hexene | 0.2201 | 0.0902 | 0.1161 | 0.2183 | 0.1183 |
| Cis-3-hexene | 0.1415 | 0.0512 | 0.0609 | 0.1110 | 0.0668 |
| 2-Me-1-pentene | 0.1402 | 0.0555 | 0.0564 | 0.1201 | 0.0770 |
| 4-methyl-1-pentene | 0.0826 | 0.0241 | 0.0260 | 0.0509 | 0.0405 |
| 2-methyl-2-pentene | 0.2949 | 0.1812 | 0.2331 | 0.4399 | 0.2275 |
| C-3Me-2-pentene | 0.1145 | 0.0412 | 0.0398 | 0.0779 | 0.0580 |
| T-3Me-2-pentene | 0.1795 | 0.0626 | 0.0624 | 0.1216 | 0.0876 |
| C-4Me-2-pentene | 0.0329 | 0.0151 | 0.0205 | 0.0466 | 0.0267 |
| T-4Me-2-pentene | 0.1404 | 0.0733 | 0.1167 | 0.3096 | 0.1267 |
| 2-Et-1-butene | 0.0426 | 0.0150 | 0.0118 | 0.0277 | 0.0207 |
| 2,3dimethyl-1-butene | 0.0444 | 0.0000 | 0.0030 | 0.0425 | 0.0016 |
| 3,3-dimethylbutene | 0.0051 | 0.0013 | 0.0018 | 0.0019 | 0.0022 |
| 2,3dimethyl-2-butene | 0.0545 | 0.0314 | 0.0404 | 0.0681 | 0.0390 |
| Nonenes | 0.0053 | 0.0026 | 0.0076 | 0.0067 | 0.0041 |
| Cyclopentene | 0.1159 | 0.0396 | 0.0373 | 0.0390 | 0.0568 |
| 1-Me-cyclopentene | 0.2562 | 0.0812 | 0.0565 | 0.0982 | 0.0926 |
| 3-Me-cyclopentene | 0.0731 | 0.0207 | 0.0132 | 0.0242 | 0.0287 |
| 23-diMe-1-pentene | 0.0206 | 0.0080 | 0.0064 | 0.0097 | 0.0070 |
| 24-dime-1-pentene | 0.0151 | 0.0054 | 0.0035 | 0.0053 | 0.0036 |
| 23Dimethyl-2-Pentene | 0.0012 | 0.0000 | 0.0000 | 0.0002 | 0.0000 |
| 33-DiMe-1-pentene | 0.0039 | 0.0000 | 0.0008 | 0.0018 | 0.0005 |
| 44-diMe-1-pentene | 0.0326 | 0.0070 | 0.0052 | 0.0092 | 0.0083 |

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| | | | | | |
| 23-diMe-2-pentene | 0.0679 | 0.0288 | 0.0219 | 0.0339 | 0.0279 |
| 24Dimethyl-2-Pentene | 0.0044 | 0.0000 | 0.0005 | 0.0013 | 0.0000 |
| 34-diMe-c2-pentene | 0.0273 | 0.0117 | 0.0039 | 0.0060 | 0.0000 |
| 44-diMe-c2-pentene | 0.0100 | 0.0030 | 0.0018 | 0.0033 | 0.0029 |
| 3-Et-2-pentene | 0.1524 | 0.0583 | 0.0391 | 0.0611 | 0.0555 |
| 2-Me-1-hexene | 0.0401 | 0.0159 | 0.0129 | 0.0181 | 0.0128 |
| 3-Me-1-hexene | 0.0074 | 0.0025 | 0.0017 | 0.0022 | 0.0017 |
| 5-Me-1-hexene | 0.0236 | 0.0088 | 0.0073 | 0.0112 | 0.0085 |
| 2-Me-2-hexene | 0.0746 | 0.0305 | 0.0240 | 0.0358 | 0.0282 |
| 2-Me-t3-hexene | 0.0451 | 0.0162 | 0.0126 | 0.0179 | 0.0123 |
| 3-Me-c3-hexene | 0.0516 | 0.0216 | 0.0166 | 0.0255 | 0.0205 |
| 3-Me-t3-hexene | 0.0328 | 0.0135 | 0.0102 | 0.0155 | 0.0123 |
| 1-Heptene | 0.0328 | 0.0102 | 0.0115 | 0.0151 | 0.0162 |
| Cis-2-heptene | 0.0018 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Trans-2-heptene | 0.0000 | 0.0125 | 0.0114 | 0.0051 | 0.0156 |
| T3-Heptene | 0.0676 | 0.0219 | 0.0135 | 0.0191 | 0.0087 |
| 1-Octene | 0.0150 | 0.0000 | 0.0003 | 0.0019 | 0.0033 |
| C2-Octene | 0.0303 | 0.0119 | 0.0111 | 0.0218 | 0.0141 |
| C4-Octene | 0.0602 | 0.0470 | 0.0224 | 0.0009 | 0.0000 |
| 4-M-1-Heptene | 0.0375 | 0.0410 | 0.0411 | 0.0275 | 0.0504 |
| t-4-M-2-Heptene | 0.0154 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C-2-m-3-heptene | 0.0614 | 0.1493 | 0.0000 | 0.0904 | 0.1264 |
| c-6-M-2-Heptene | 0.0055 | 0.0015 | 0.0090 | 0.0014 | 0.0016 |
| 2-Methyl-2-heptene | 0.0336 | 0.0398 | 0.0376 | 0.0290 | 0.0428 |
| 2235TetMethylhexane | 0.0069 | 0.0000 | 0.0060 | 0.0000 | 0.0000 |
| C-7 Olefin A | 0.0122 | 0.0057 | 0.0036 | 0.0070 | 0.0053 |
| C-7 Olefin B | 0.0019 | 0.0000 | 0.0003 | 0.0012 | 0.0000 |
| C-7 Olefin D | 0.0043 | 0.0012 | 0.0005 | 0.0020 | 0.0003 |
| Octene B | 0.0070 | 0.0028 | 0.0014 | 0.0029 | 0.0042 |
| Octene C | 0.0151 | 0.0073 | 0.0038 | 0.0056 | 0.0051 |
| Octene D | 0.0195 | 0.0070 | 0.0039 | 0.0073 | 0.0063 |
| Octene E | 0.0000 | 0.0000 | 0.0000 | 0.0009 | 0.0000 |
| Octene F | 0.0038 | 0.0013 | 0.0009 | 0.0021 | 0.0005 |
| Octene G | 0.0026 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Octene H | 0.0146 | 0.0056 | 0.0104 | 0.0066 | 0.0067 |
| Octene I | 0.0227 | 0.0094 | 0.0076 | 0.0104 | 0.0099 |
| C-8 Olefin K | 0.0219 | 0.0150 | 0.0130 | 0.0099 | 0.0145 |
| C-8 Olefin M | 0.0168 | 0.0289 | 0.0180 | 0.0045 | 0.0166 |
| C-7 cyclopentene A | 0.0702 | 0.0258 | 0.0156 | 0.0313 | 0.0289 |
| C-7 cyclopentene B | 0.0664 | 0.0251 | 0.0152 | 0.0305 | 0.0279 |
| 1,3-butadiene | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0000 |
| C-1,3-pentadiene | 0.0071 | 0.0030 | 0.0014 | 0.0017 | 0.0047 |
| T-1,3-pentadiene | 0.0143 | 0.0054 | 0.0028 | 0.0034 | 0.0115 |
| 1,4-pentadiene | 0.0005 | 0.0000 | 0.0002 | 0.0001 | 0.0006 |
| 2-Me-1,3-butadiene | 0.0125 | 0.0049 | 0.0029 | 0.0035 | 0.0123 |
| T-1Me-1,3-pentadiene | 0.0015 | 0.0000 | 0.0001 | 0.0000 | 0.0000 |

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|--|--|--|--|--|--|
| 1,7-Octadiene Cyclopentadiene 1-Me-cyclopentadiene Octadiene A T-2-T-4-hexadiene | 0.0020 0.0083 0.0298 0.0551 0.0096 | 0.0000 0.0072 0.0207 0.0227 0.0032 | 0.0010 0.0068 0.0110 0.0153 0.0017 | 0.0003 0.0029 0.0032 0.0270 0.0027 | 0.0000 0.0069 0.0148 0.0316 0.0026 |
| aromatics | | | | | |
| Benzene | 1.9814 | 0.5846 | 0.5367 | 0.5402 | 0.5388 |
| Toluene | 9.7808 | 8.0011 | 6.3368 | 8.2616 | 7.8443 |
| Ethylbenzene | 2.1127 | 1.5637 | 1.4841 | 1.4930 | 1.5225 |
| o-Xylene | 3.0394 | 2.2864 | 2.0803 | 2.2625 | 2.3618 |
| m-Xylene | 6.8078 | 5.0374 | 4.3582 | 4.9076 | 5.0386 |
| p-Xylene | 1.5958 | 1.4405 | 1.2670 | 1.3417 | 1.4461 |
| Cumene | 0.1286 | 0.0898 | 0.1029 | 0.0945 | 0.1069 |
| 1-Me-2-Et-benzene | 0.7574 | 0.4914 | 0.5349 | 0.5322 | 0.5864 |
| 1-Me-3-Et-benzene | 2.2810 | 1.4582 | 1.5342 | 1.5624 | 1.7024 |
| 1-Me-4-Et-benzene | 0.9865 | 0.6470 | 0.6829 | 0.6879 | 0.7503 |
| 123-triMe-benzene | 0.6751 | 0.4580 | 0.4909 | 0.5253 | 0.5626 |
| 124-TriMe-benzene | 3.4686 | 2.3502 | 2.4198 | 2.6349 | 2.7962 |
| 135-triMe-benzene | 1.1534 | 0.7534 | 0.7929 | 0.8033 | 0.8509 |
| Butylbenzene | 0.1370 | 0.0535 | 0.1050 | 0.0540 | 0.0877 |
| Isobutylbenzene | 0.0891 | 0.0616 | 0.0882 | 0.0707 | 0.0693 |
| Sec-butylbenzene | 0.0746 | 0.0322 | 0.0591 | 0.0403 | 0.0589 |
| o-Cymene | 0.0329 | 0.0272 | 0.0270 | 0.0075 | 0.0192 |
| m-Cymene | 0.0871 | 0.0446 | 0.0709 | 0.0595 | 0.0816 |
| p-Cymene | 0.0241 | 0.0135 | 0.0221 | 0.0186 | 0.0264 |
| 1234-tetMe-benzene | 0.1214 | 0.0640 | 0.0711 | 0.0714 | 0.0704 |
| 1235-tetMe-benzene | 0.3969 | 0.1922 | 0.2356 | 0.2306 | 0.2274 |
| 1245-tetMe-benzene | 0.3080 | 0.1454 | 0.1832 | 0.1785 | 0.1772 |
| Pentamethylbenzene | 0.0275 | 0.0112 | 0.0144 | 0.0135 | 0.0144 |
| Propylbenzene | 0.6606 | 0.4489 | 0.5650 | 0.4571 | 0.5107 |
| 1,3-diethylbenzene | 0.2058 | 0.0811 | 0.1259 | 0.1114 | 0.1260 |
| 1-Me-3-Pr-benzene | 0.5369 | 0.1932 | 0.3234 | 0.2777 | 0.3124 |
| 1-Me-4-Pr-benzene | 0.3132 | 0.1179 | 0.2082 | 0.1870 | 0.1925 |
| Indan | 0.4156 | 0.1998 | 0.2622 | 0.2359 | 0.2820 |
| 1,2-diethylbenzene | 0.5890 | 0.2553 | 0.3707 | 0.3419 | 0.3649 |
| 1-Me-2-Pr-benzene | 0.1625 | 0.0659 | 0.1228 | 0.0908 | 0.1042 |
| 14-diMe2Et-benzene | 0.3978 | 0.1701 | 0.2358 | 0.2326 | 0.2619 |
| 13-diMe4Et-benzene | 0.3229 | 0.1459 | 0.2066 | 0.1981 | 0.2111 |
| 12-diMe4Et-benzene | 0.5428 | 0.2268 | 0.3046 | 0.3034 | 0.3299 |
| 13-diMe2Et-benzene | 0.0356 | 0.0213 | 0.0278 | 0.0271 | 0.0262 |
| Indene | 0.0112 | 0.0000 | 0.0439 | 0.0335 | 0.0334 |
| 12-diMe3Et-benzene | 0.1576 | 0.0627 | 0.0925 | 0.0841 | 0.0938 |
| 1-Me35diEt-benzene | 0.0688 | 0.0170 | 0.0395 | 0.0290 | 0.0289 |
| 1-Phenyl-2Me butane | 0.0530 | 0.0244 | 0.0424 | 0.0310 | 0.0296 |
| 1-Phenyl-3Me butane | 0.0090 | 0.0149 | 0.0152 | 0.0116 | 0.0044 |

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|--------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| 124-triMe-5Etbenzene | 0.0477 | 0.0174 | 0.0235 | 0.0203 | 0.0213 |
| 123-triMe-5Etbenzene | 0.0545 | 0.0132 | 0.0229 | 0.0175 | 0.0236 |
| 124-triMe-3Etbenzene | 0.0091 | 0.0010 | 0.0017 | 0.0012 | 0.0014 |
| 12-diMe-3Pr-benzene | 0.0969 | 0.0298 | 0.0430 | 0.0331 | 0.0368 |
| 135-triMe-2Etbenzene | 0.0207 | 0.0180 | 0.0178 | 0.0151 | 0.0134 |
| Naphthalene | 0.4808 | 0.1306 | 0.1903 | 0.1376 | 0.1279 |
| Tetralin | 0.0279 | 0.0000 | 0.0001 | 0.0096 | 0.0326 |
| cis-Decalin | 0.0000 | 0.0000 | 0.0030 | 0.0000 | 0.0000 |
| 1-Me-3Bu-benzene | 0.0824 | 0.0371 | 0.0627 | 0.0355 | 0.0326 |
| 12-diMe-4Pr-benzene | 0.0424 | 0.0463 | 0.0342 | 0.0426 | 0.0304 |
| 125-triMe-3Etbenzene | 0.0700 | 0.0232 | 0.0336 | 0.0281 | 0.0308 |
| 123-triMe4Et-benzene | 0.0176 | 0.0060 | 0.0054 | 0.0089 | 0.0096 |
| C-11 Aromatic K | 0.0277 | 0.0204 | 0.0080 | 0.0159 | 0.0138 |
| C-10 Alkenylbenzenes | 0.0165 | 0.0000 | 0.0488 | 0.0011 | 0.0058 |
| C-11 Aromatic L | 0.0000 | 0.0000 | 0.0071 | 0.0005 | 0.0000 |
| 1-Methylnaphthalene | 0.1513 | 0.0276 | 0.0758 | 0.0423 | 0.0401 |
| 2-Methylnaphthalene | 0.3304 | 0.0698 | 0.1668 | 0.0900 | 0.0860 |
| C-11 Aromatic E | 0.1243 | 0.0381 | 0.0614 | 0.0497 | 0.0553 |
| C-12 Aromatic A | 0.0068 | 0.0000 | 0.0015 | 0.0009 | 0.0000 |
| C-12 Aromatic F | 0.0130 | 0.0035 | 0.0057 | 0.0029 | 0.0031 |
| 1-Methylindane | 0.2248 | 0.0700 | 0.1020 | 0.0816 | 0.0962 |
| 2-Methylindane | 0.3631 | 0.1116 | 0.1594 | 0.1262 | 0.1472 |
| Dimethylindane A | 0.0269 | 0.0134 | 0.0091 | 0.0080 | 0.0112 |
| Dimethylindane B | 0.0660 | 0.0224 | 0.0183 | 0.0164 | 0.0269 |
| Dimethylindane C | 0.0353 | 0.0119 | 0.0113 | 0.0102 | 0.0151 |
| Dimethylindane E | 0.0460 | 0.0138 | 0.0127 | 0.0127 | 0.0189 |
| Dimethylindane F | 0.0727 | 0.0223 | 0.0334 | 0.0220 | 0.0250 |
| Dimethylindane G | 0.0477 | 0.0104 | 0.0218 | 0.0124 | 0.0198 |
| C-11 Indane H | 0.0364 | 0.0086 | 0.0161 | 0.0081 | 0.0116 |
| Biphenyl | 0.0000 | 0.0000 | 0.0055 | 0.0000 | 0.0000 |
| 12-DiMe-naphthalene | 0.0080 | 0.0006 | 0.0053 | 0.0032 | 0.0029 |
| 13-DiMe-naphthalene | 0.0407 | 0.0083 | 0.0299 | 0.0153 | 0.0129 |
| 15-DiMe-naphthalene | 0.0000 | 0.0000 | 0.0000 | 0.0005 | 0.0000 |
| 16-DiMe-naphthalene | 0.0190 | 0.0047 | 0.0147 | 0.0078 | 0.0060 |
| 23-DiMe-naphthalene | 0.0183 | 0.0043 | 0.0140 | 0.0076 | 0.0057 |
| 26-DiMe-naphthalene | 0.0000 | 0.0000 | 0.0012 | 0.0031 | 0.0019 |
| 27-DiMe-naphthalene | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0000 |
| 1-Ethylnaphthalene | 0.0128 | 0.0022 | 0.0112 | 0.0054 | 0.0032 |
| 2-Ethylnaphthalene | 0.0000 | 0.0000 | 0.0000 | 0.0023 | 0.0017 |
| 235-TriMeNaphthalene | 0.0000 | 0.0000 | 0.0028 | 0.0006 | 0.0000 |

| wt% in Liquid Gasoline Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|--------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| oxygenates | | | | | |
| Ethanol | 0.0000 | 0.0000 | 0.0000 | 1.2526 | 0.8622 |
| 2-methyl-2-propanol | 0.0000 | 0.0000 | 0.0071 | 0.0039 | 0.0046 |
| 2-methyl-2-butanol | 0.0000 | 0.0000 | 0.0023 | 0.0037 | 0.0000 |
| MTBE | 0.9939 | 10.9139 | 8.5808 | 3.8286 | 10.5669 |
| TAME | 0.0393 | 0.0170 | 1.0652 | 0.6054 | 0.4164 |
| 3-Me-3-methoxypentane | 0.0000 | 0.0000 | 0.0002 | 0.0000 | 0.0000 |
| 1-Me-1methoxycyclpen | 0.0000 | 0.0000 | 0.0037 | 0.0000 | 0.0000 |
| 2-Methoxybutane | 0.0000 | 0.0000 | 0.0021 | 0.0013 | 0.0040 |
| unclassified | 1.5416 | 1.3297 | 1.8381 | 1.2557 | 1.3293 |

| wt% in Headspace Vapors Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|---------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| n-alkanes | | | | | |
| Propane | 1.03 | 0.28 | 0.46 | 0.38 | 0.64 |
| Butane | 9.96 | 6.28 | 9.84 | 7.97 | 8.90 |
| Pentane | 9.34 | 7.27 | 7.15 | 8.75 | 8.52 |
| Hexane | 1.88 | 1.43 | 1.35 | 1.65 | 1.82 |
| Heptane | 0.42 | 0.39 | 0.47 | 0.48 | 0.51 |
| Octane | 0.05 | 0.05 | 0.07 | 0.05 | 0.07 |
| Nonane | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| isoalkanes | | | | | |
| 2-methylpropane | 3.28 | 1.30 | 1.25 | 0.96 | 2.43 |
| 2-methylbutane | 37.05 | 34.86 | 35.78 | 37.30 | 29.82 |
| 2,2-dimethylpropane | 0.08 | 0.10 | 0.13 | 0.04 | 0.06 |
| 2-methylpentane | 5.75 | 5.56 | 5.39 | 6.13 | 4.68 |
| 3-methylpentane | 3.28 | 3.05 | 2.96 | 3.33 | 2.59 |
| 2,2-dimethylbutane | 1.81 | 1.55 | 2.40 | 2.55 | 1.81 |
| 2,3-dimethylbutane | 1.55 | 1.95 | 2.19 | 2.34 | 1.64 |
| 2-methylhexane | 0.79 | 0.67 | 0.62 | 0.70 | 0.66 |
| 3-methylhexane | 0.81 | 0.73 | 0.73 | 0.82 | 0.79 |
| 3-ethylpentane | 0.07 | 0.04 | 0.03 | 0.03 | 0.05 |
| 2,2-dimethylpentane | 0.10 | 0.06 | 0.07 | 0.08 | 0.08 |
| 2,3-dimethylpentane | 0.45 | 0.64 | 0.77 | 0.96 | 0.80 |
| 2,4-dimethylpentane | 0.32 | 0.49 | 0.57 | 0.60 | 0.48 |
| 33-Dimethylpentane | 0.08 | 0.06 | 0.00 | 0.06 | 0.06 |
| 223-Trimethylbutane | 0.00 | 0.03 | 0.00 | 0.03 | 0.02 |
| 2-Methylheptane | 0.09 | 0.12 | 0.12 | 0.11 | 0.13 |
| 3-methylheptane | 0.11 | 0.12 | 0.12 | 0.11 | 0.12 |
| 4-Methylheptane | 0.05 | 0.06 | 0.06 | 0.05 | 0.06 |
| 2,2-dimethylhexane | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 2,4-dimethylhexane | 0.07 | 0.13 | 0.14 | 0.13 | 0.09 |
| 2,5-dimethylhexane | 0.06 | 0.12 | 0.15 | 0.12 | 0.08 |
| 3,3-dimethylhexane | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 2-Me-3-Et-pentane | 0.05 | 0.10 | 0.11 | 0.10 | 0.07 |
| 2,4-dimethylheptane | 0.01 | 0.02 | 0.01 | 0.01 | 0.00 |
| 2,6-dimethylheptane | 0.01 | 0.01 | 0.02 | 0.01 | 0.02 |
| 2,5-dimethylheptane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3,5-dimethylheptane | 0.02 | 0.03 | 0.03 | 0.02 | 0.03 |
| 2,3-dimethylheptane | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 3,4-dimethylheptane | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| 3,3-dimethylheptane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4,4-dimethylheptane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2,2-dimethylheptane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3-Me-4-Et-hexane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 223-triMe-pentane | 0.02 | 0.04 | 0.05 | 0.04 | 0.03 |
| 224-triMe-pentane | 0.30 | 1.21 | 1.36 | 1.23 | 0.65 |
| 233-triMe-pentane | 0.09 | 0.31 | 0.39 | 0.33 | 0.18 |
| • | | | | | |

| wt% in Headspace Vapors Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|--|------------------|------------------|------------------|------------------|--------------------|
| 224 triMo poptano | 0.08 | 0.31 | 0.38 | 0.33 | 0.18 |
| 234-triMe-pentane 225-trimethylhexane | 0.08 | 0.31 | 0.38 | 0.33 | 0.18 |
| 235-trimethylhexane | 0.02 | 0.12 | 0.07 | 0.13 | 0.03 |
| 244-trimethylhexane | 0.01 | 0.02 | 0.01 | 0.02 | 0.01 |
| 223-trimethylhexane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 223 timetrymexane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| cycloalkanes (naphthenes) | | | | | |
| Cyclopentane | 1.06 | 0.98 | 0.90 | 0.99 | 0.98 |
| Methylcyclopentane | 2.20 | 2.63 | 1.89 | 2.44 | 2.40 |
| Ethylcyclopentane | 0.05 | 0.07 | 0.07 | 0.07 | 0.10 |
| 1,1-diMecyclopentane | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1T2-diMecyclopentane | 0.18 | 0.17 | 0.20 | 0.22 | 0.27 |
| 1C3-diMecyclopentane | 0.25 | 0.23 | 0.23 | 0.26 | 0.31 |
| 1T3-diMecyclopentane | 0.21 | 0.19 | 0.20 | 0.22 | 0.27 |
| Propylcyclopentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 112-triMeCyPentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 113-triMeCyPentane | 0.02 | 0.03 | 0.03 | 0.03 | 0.04 |
| 1C2C3-triMeCypentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1C2T3-triMeCyPentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1T2C3-triMeCyPentane | 0.01 | 0.02 | 0.03 | 0.02 | 0.03 |
| 1C2C4-triMeCyPentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1T2C4-triMeCyPentane | 0.02 | 0.04 | 0.05 | 0.03 | 0.05 |
| 1Me-1EtCyclopentane | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 |
| 1Me-C2EtCyclopentane | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 |
| 1MeC3EtCyclopentane | 0.01 | 0.02 | 0.02 | 0.01 | 0.02 |
| 1-M-t-3-Et Cycpentane | 0.01 | 0.02 | 0.02 | 0.01 | 0.02 |
| Cyclohexane | 0.57 | 0.89 | 0.71 | 1.06 | 1.02 |
| Methylcyclohexane | 0.32 | 0.38 | 0.47 | 0.47 | 0.56 |
| Ethylcyclohexane | 0.00 | 0.01 | 0.02 | 0.01 | 0.02 |
| 1,1-diMecyclohexane | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 |
| 1C2-diMecyclohexane | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| 1T2-diMecyclohexane | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 |
| 1C3-diMecyclohexane | 0.01 | 0.04 | 0.05 | 0.03 | 0.04 |
| 1T3-diMecyclohexane | 0.01 | 0.03 | 0.02 | 0.02 | 0.02 |
| 1C4-diMecyclohexane | 0.01 | 0.00 | 0.02 | 0.00 | 0.01 |
| alkenes (olefins) | | | | | |
| 1-butene | 0.23 | 0.12 | 0.09 | 0.05 | 0.09 |
| Cis-2-butene | 0.41 | 0.34 | 0.25 | 0.13 | 0.21 |
| Trans-2-butene | 0.40 | 0.59 | 0.37 | 0.26 | 0.27 |
| 2-methylpropene | 0.27 | 0.16 | 0.07 | 0.05 | 0.14 |
| 1-pentene | 0.83 | 0.21 | 0.16 | 0.17 | 0.38 |
| Cis-2-pentene | 0.74 | 0.30 | 0.23 | 0.28 | 0.36 |
| trans-2-pentene | 1.35 | 0.73 | 0.54 | 0.64 | 0.75 |
| 2-methyl-1-butene | 1.15 | 0.41 | 0.18 | 0.38 | 0.61 |
| 3-methyl-1-butene | 0.34 | 0.08 | 0.11 | 0.07 | 0.15 |
| , | - | | | - | _ |

| wt% in Headspace Vapors Name | Berkeley 1995 | Berkeley 1996 | Berkeley 1999 | Berkeley 2001 | Sacramento 2001 |
|---------------------------------|------------------|------------------|------------------|------------------|--------------------|
| | | | | | |
| 2-methyl-2-butene | 1.75 | 1.02 | 0.39 | 1.08 | 1.11 |
| 1-hexene | 0.12 | 0.03 | 0.03 | 0.04 | 0.04 |
| Cis-2-hexene | 0.11 | 0.04 | 0.04 | 0.08 | 0.05 |
| Trans-2-hexene | 0.22 | 0.09 | 0.12 | 0.21 | 0.12 |
| Cis-3-hexene | 0.14 | 0.05 | 0.06 | 0.11 | 0.07 |
| 2-Me-1-pentene | 0.16 | 0.06 | 0.06 | 0.13 | 0.09 |
| 4-methyl-1-pentene | 0.09 | 0.03 | 0.03 | 0.06 | 0.04 |
| 2-methyl-2-pentene | 0.29 | 0.18 | 0.24 | 0.43 | 0.22 |
| C-3Me-2-pentene | 0.11 | 0.04 | 0.04 | 0.08 | 0.06 |
| T-3Me-2-pentene | 0.16 | 0.06 | 0.06 | 0.11 | 0.08 |
| C-4Me-2-pentene | 0.05 | 0.02 | 0.03 | 0.07 | 0.04 |
| T-4Me-2-pentene | 0.19 | 0.10 | 0.16 | 0.42 | 0.17 |
| 2-Et-1-butene | 0.06 | 0.02 | 0.02 | 0.04 | 0.03 |
| 2,3dimethyl-1-butene | 0.07 | 0.00 | 0.00 | 0.06 | 0.00 |
| 3,3-dimethylbutene | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2,3dimethyl-2-butene | 0.04 | 0.03 | 0.03 | 0.05 | 0.03 |
| Cyclopentene | 0.26 | 0.09 | 0.09 | 0.09 | 0.13 |
| 1-Me-cyclopentene | 0.14 | 0.05 | 0.03 | 0.05 | 0.05 |
| 3-Me-cyclopentene | 0.04 | 0.01 | 0.01 | 0.01 | 0.02 |
| 23-diMe-1-pentene | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 |
| 24-dime-1-pentene | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| 23Dimethyl-2-Pentene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 33-DiMe-1-pentene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 44-diMe-1-pentene | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 |
| 23-diMe-2-pentene | 0.04 | 0.02 | 0.01 | 0.02 | 0.02 |
| 24Dimethyl-2-Pentene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 34-diMe-c2-pentene | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 |
| 44-diMe-c2-pentene | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3-Et-2-pentene | 0.08 | 0.03 | 0.02 | 0.03 | 0.03 |
| 2-Me-1-hexene | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| 3-Me-1-hexene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5-Me-1-hexene | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 |
| 2-Me-2-hexene | 0.04 | 0.02 | 0.01 | 0.02 | 0.02 |
| 2-Me-t3-hexene | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 |
| 3-Me-c3-hexene | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 |
| 3-Me-t3-hexene | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| 1-Heptene | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| Cis-2-heptene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Trans-2-heptene | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| T3-Heptene | 0.04 | 0.01 | 0.01 | 0.01 | 0.00 |
| C-7 Olefin A | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| C-7 Olefin B | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C-7 Olefin D | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C-7 cyclopentene A | 0.04 | 0.01 | 0.01 | 0.02 | 0.02 |
| C-7 cyclopentene B | 0.04 | 0.01 | 0.01 | 0.02 | 0.02 |
| 1,3-butadiene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | | | |

| wt% in Headspace Vapors | Berkeley | Berkeley | Berkeley | Berkeley | Sacramento |
|-------------------------|----------|----------|----------|----------|------------|
| Name | 1995 | 1996 | 1999 | 2001 | 2001 |
| | | | | | |
| C-1,3-pentadiene | 0.02 | 0.01 | 0.00 | 0.00 | 0.01 |
| T-1,3-pentadiene | 0.03 | 0.01 | 0.01 | 0.01 | 0.03 |
| 1,4-pentadiene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2-Me-1,3-butadiene | 0.04 | 0.02 | 0.01 | 0.01 | 0.04 |
| T-1Me-1,3-pentadiene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cyclopentadiene | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 |
| 1-Me-cyclopentadiene | 0.04 | 0.03 | 0.02 | 0.00 | 0.02 |
| T-2-T-4-hexadiene | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | | | |
| aromatics | | | | | |
| Benzene | 1.21 | 0.36 | 0.34 | 0.36 | 0.35 |
| Toluene | 1.92 | 1.59 | 1.28 | 1.72 | 1.60 |
| Ethylbenzene | 0.15 | 0.11 | 0.11 | 0.11 | 0.11 |
| o-Xylene | 0.15 | 0.12 | 0.11 | 0.12 | 0.12 |
| m-Xylene | 0.42 | 0.32 | 0.28 | 0.32 | 0.32 |
| p-Xylene | 0.10 | 0.09 | 0.08 | 0.09 | 0.10 |
| | | | | | |
| oxygenates | | | | | |
| Ethanol | 0.00 | 0.00 | 0.00 | 1.79 | 1.22 |
| 2-methyl-2-propanol | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MTBE | 1.54 | 16.82 | 13.40 | 5.78 | 15.97 |
| TAME | 0.02 | 0.01 | 0.41 | 0.23 | 0.16 |
| 2-Methoxybutane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |